# THERMAL, ELECTRICAL

# AND

# MAGNETIC PROPERTIES OF ALLOYS

BY

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# THERMAL, ELECTRICAL AND MAGNETIC PROPERTIES OF ALLOYS.*

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## INTRODUCTION.

THE physical properties of alloys including hardness, conductivity for heat and electricity, thermoelectric power, magnetic susceptibility, rate of change of resistance with the temperature, etc., are intimately connected with the constitution of the alloys. In the absence of intermetallic compounds the physical properties are in general continuous functions of the composition for any given series of alloys. The physical property may be a linear function of the concentration as is ordinarily the case in conglomerates or it may pass through a maximum or a minimum as in alloys formed of metals which are mutually soluble in each other in all proportions. Discontinuities may occur in cases of limited solubility in the solid state and the curve which represents the variation of the physical property with the composition then shows an abrupt change in direction at the concentration at which one metal ceases to be soluble in the other. In case the metals entering into the alloys form one or more intermetallic compounds the alloys will have a new set of physical properties at the point at which the concentration of the compound is a maximum.

For the purposes of this study of the relation between the thermal, electrical and magnetic properties of alloys and their constitution alloys may be divided into five groups.

I. The two components are not soluble in each other and form no chemical compounds with each other. A metallographic study shows that the alloys in this case are mechanical mixtures of the two components. The lead-cadmium series is an example of this type of alloys. In such alloys the physical property is usually a linear function of the concentration of one of the components. For example, the electrical conductivity of a series of such conglomerates is represented by Curve I of Fig. 1.

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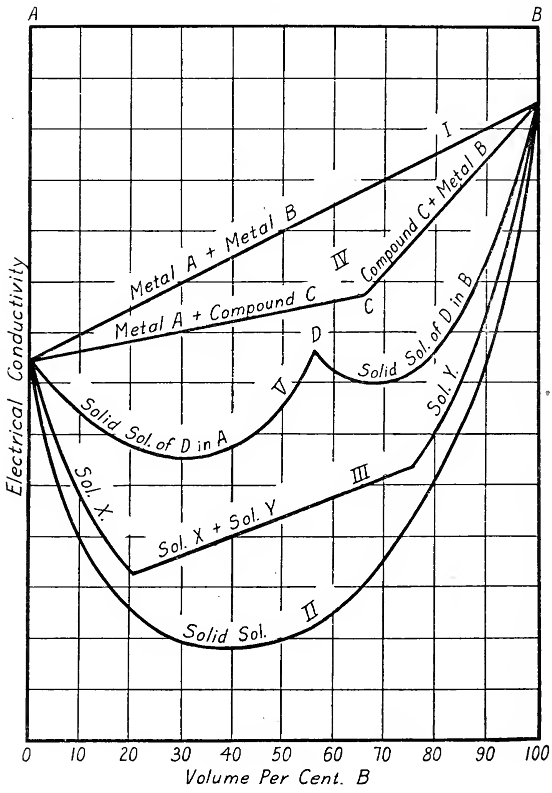
II. The two components are soluble in each other in all proportions, *i.e.*, they form by varying the concentration of one of the components an unbroken series of mixed crystals. Alloys of palladium with silver or nickel with copper belong to this group. A curve representing the physical property as a function of the con-

FIG. I.




centration of one of the components is characterized by a pronounced maximum or minimum. The electrical conductivity when plotted as a function of the concentration of one of the components gives in this case a curve of the form of Curve II of Fig. I.

III. Each of the components is soluble in the other to a lim-

ited extent. The alloys of this series will then consist of three parts, solid solutions of the first component in the second, solid solutions of the second component in the first and mechanical mixtures of saturated solutions of the first component in the second with saturated solutions of the second component in the first. A typical curve for such a property as the electrical conductivity of alloys of this group is represented in Curve III of Fig. 1. It consists of three parts, a central portion which is linear where there is a mechanical mixture of one saturated solution in another and on either side of this a portion which is similar to the initial and final parts of Curve II.

IV. The two metals *A* and *B* form a single compound *C* (Curve IV, Fig. 1) and this compound forms mechanical mixtures both with *A* and *B*. The curve representing the physical property consists of two straight lines intersecting at *C*.

V. The components form one or more intermetallic compounds. Bismuth-tellurium alloys furnish an example of this group. In this case the curves, showing the physical properties as a function of the concentration of one of the components, may assume a variety of forms according to the nature of the intermetallic compound. If the compound happens to form solid solutions with both of the components in the alloys the curve will take the form of Curve V of Fig. 1. In that case a compound *D* was formed which formed solid solutions with both *A* and *B*.

#### PHYSICAL QUANTITIES AND UNITS.

The specific resistance has been taken to mean the resistance in ohms or in microöhms of a wire one centimetre in cross section and one centimetre in length. The electrical conductivity is understood to be the reciprocal of the specific resistance, and it has been expressed as the reciprocal of ohms for which the term mho has been used.

The temperature coefficient of the resistance has been considered to be the rate of change of the resistance per ohm per degree Centigrade.

By the thermal conductivity is understood the quantity of heat in calories which will flow in one second through an area of one square centimetre when the temperature gradient is one degree Centigrade per centimetre.

The thermoelectric power has been measured against lead except in a few cases where it has been measured against platinum. These exceptions are clearly indicated on the figures. The thermoelectric power has been expressed as the number of microvolts for a difference of one degree Centigrade between the junctions. For the rate of variation of the thermoelectric power with the temperature the Centigrade scale has also been used.

The Thomson coefficient, which is a measure of the heat absorbed or evolved in excess of the Joulean heat by a current of electricity flowing along an unequally heated conductor, has been measured in ergs. It gives the amount of heat in ergs which is absorbed or generated in excess of Joulean heat by a current of one absolute unit flowing through a conductor in which there is a temperature gradient of one degree Centigrade per centimetre.

In the Hall constant which is a measure of the rotation of the equipotential lines under the action of a transverse magnetic field, the electric current, the transverse difference of potential and the magnetic field have been measured in absolute units and the thickness of the plate in centimetres. This constant is defined by the equation,

$$E = R\frac{Hi}{d}$$

where $E$ = the transverse electromotive force produced by the magnetic action.

$H$ = the intensity of the magnetic field.
$i$ = the current in the plate.
$d$ = the thickness of the plate.
$R$ = the Hall constant.

For paramagnetic and diamagnetic substances the relation between the intensity of magnetization and the magnetic field which produces it may be expressed by the equation,

$$I = kH.$$

where $H$ = the magnetic field in gausses.
$k$ = the magnetic susceptibility per unit volume.

Sometimes the magnetic susceptibility per unit mass is used. In such a case it is called the specific magnetic susceptibility and is defined by the relation,

$$\chi = \frac{k}{\rho},$$

where $\rho$ = density of the substitute.

To get a measure of the elastic properties of the alloys it has been necessary to accept the data on these properties in a variety of forms. In some cases the hardness on Brinell's scale has been used; in others the pressure necessary to cause the metal or alloy to flow, and in others the tensible strength. There is no simple way of passing from one of these kinds of data to the other. They all give some measure of the cohesive forces with which the metals and alloys are held together, and that was all that was needed in this connection.

Above the freezing point curve an attempt has been made to indicate the manner in which the metals mix to form the alloys (see Guertler, "Metallographie"). Where the alloys are mechanical mixtures for all concentrations of the constituents, this fact has been indicated by placing a plus sign between the chemical symbols of the constituents. For example $Zn + Sn$ means that tin and zinc are mechanical mixtures in all proportions. In case the metals $A$ and $B$ form an unbroken series of solid solutions, this has been indicated by writing *Sol–A–B* above the freezing point curve. If one metal $A$ is soluble to a limited extent in the other $B - a$ saturated solid solution of $A$ in $B$ has been denoted by $I$ and a saturated solid solution of $B$ in $A$ by $II$. Where these saturated solid solutions then mix mechanically to form the remainder of the alloys, this fact has been indicated by $I + II$. For example in the case of the copper-silver series, the numerals above the freezing point curve indicated that copper dissolves about 3 per cent. silver, and that silver dissolves about 5 per cent. copper. These saturated solid solutions then mix mechanically to form the remainder of the alloys.

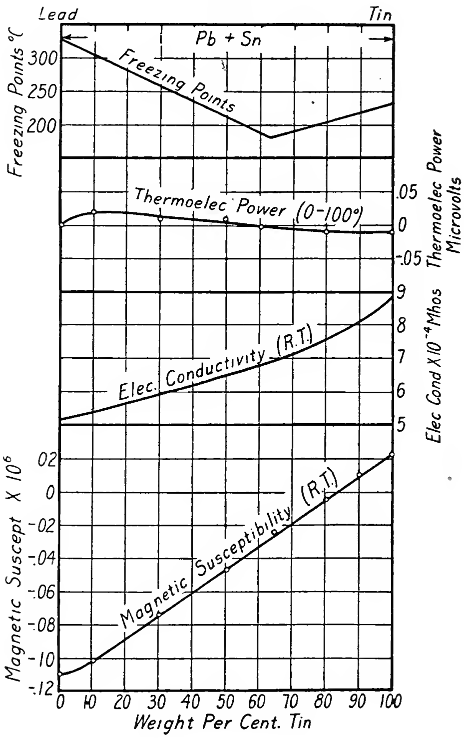
The temperature at which the observations were made or the interval of temperature over which they were made has been given on the curves as far as possible. In a number of cases the temperatures at which the observations were made were not clearly given by the observer. This is especially true for observations made in the neighborhood of room temperature. Where the observations were made near room temperature the letters (*R.T.*) have been written on the curves to indicate that fact.

## METALS INSOLUBLE IN EACH OTHER.

### *Lead-Tin.*

The freezing point curve by Degens[1] (Fig. 2) for lead-tin alloys shows a eutectic but no evidence of compounds. Tin seems to be somewhat soluble in lead and possibly lead is to a small

FIG. 2.




degree soluble in tin. Between low and high concentrations of tin the alloys are heterogeneous mixtures of the crystalline phases.

The electrical conductivities as measured by Roberts[2] give nearly a straight line as is to be expected from the fact that the alloys are heterogeneous mixtures of the components. The thermo-

[1] Degens: *Zeit. anorg. Chem.*, 63, 207, 1909.

[2] Roberts: *Phil. Mag.* (5), 8, 57, 1879.

electric powers have been determined by Rudolfi [3] and his results plotted in Fig. 2. The diamagnetic susceptibility by Honda [4] gives a curve which is nearly a straight line beginning with the value in lead and ending with the value in tin. In the alloys rich in lead (between 0 and 10 per cent. tin) where a solid solution is formed, the susceptibility decreases somewhat less rapidly than the linear relation requires. The linear relation between susceptibility and concentration follows at once from the fact that except for low and possibly high concentrations of tin the alloys are mechanical mixtures of the components.

*Tin-Zinc.*

The two branches of the freezing point curve (Fig. 3) by Heycock and Neville [5] meet at the eutectic. The changes in curvature are all gradual and there is no evidence of compounds. The alloys consist of heterogeneous mixtures of tin and zinc.

Measurements of the electrical conductivity have been made by Matthiessen,[6] Vogt,[7] Harris and Le Chatelier.[8] More recently Schulze [9] has studied both the thermal and the electrical conductivities. His observations have been plotted in Fig. 3. The temperature coefficient is from the work of Matthiessen and Vogt. Besides the observations of Rudolfi [3] on the thermoelectric heights there are earlier observations by Rollmann and Battelli.[10] The observations of Rudolfi have been used for the curve of thermoelective forces. Except for minor variations these curves are essentially linear and typical of alloys which are formed by mechanically mixing the constituents.

*Bismuth-Cadmium.*

The freezing point curve (Fig. 4) by Stoffel [11] is composed of two branches meeting at the eutectic for which the temperature

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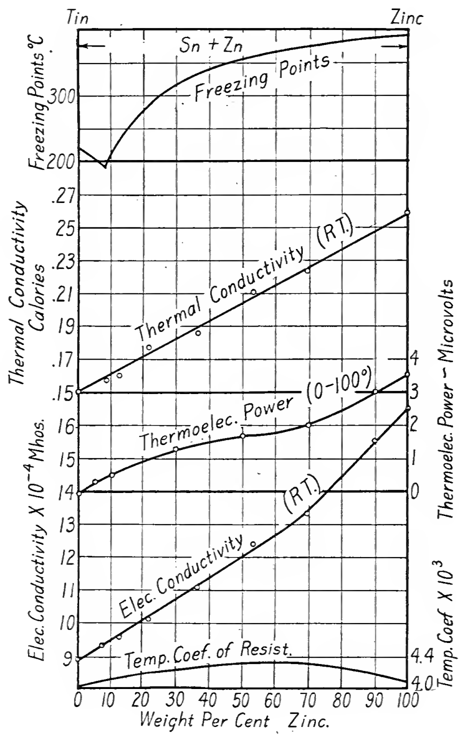
[3] Rudolfi: *Zeit. anorg. Chem.*, **67**, 65, 1910.
[4] Honda: *Sci. Rept. Tokio Univ.*, **2**, 11, 1913.
[5] Heycock and Neville: *Jour. Chem. Soc.*, **71**, 383, 1897.
[6] Matthiessen: *Pogg. Ann.*, **110**, 207, 1860.
[7] Vogt: *Pogg. Ann.*, **122**, 19, 1864.
[8] Le Chatelier: *Rev. Gen. des Sci.*, **6**, 529, 1895.
[9] Schulze: *Ann. d. Phys.*, **9**, 555, 1902.
[10] Battelli: *Atti. R. Inst. Ver.* (6), **5**, 1886–7.
[11] Stoffel: *Zeir. anorg. Chem.*, **53**, 137, 1907.

is 148° C. In all proportions the alloys are heterogeneous mixtures of bismuth and cadmium.

The thermoelectric powers by Rudolfi [12] and the magnetic susceptibility by Gnesotto and Binghinnotto [13] give curves which have the form to be expected in heterogeneous mixtures. Each of these curves by their steepness where the concentration of bismuth is

FIG. 3.




large suggests that cadmium is to a limited extent soluble in bismuth. There is some evidence from the study of the homogeneity of these alloys that cadmium may be soluble in bismuth up to about 1 per cent.

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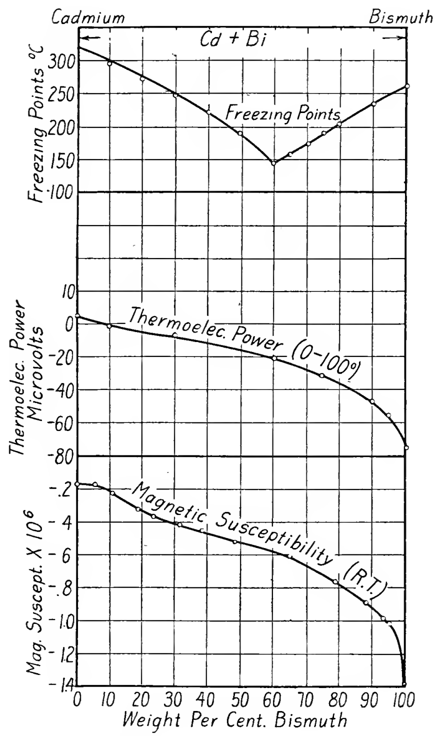
[12] Rudolfi: *Zeit. anorg. Chem.*, 67, 65, 1910.

[13] Gnesotto and Binghinnotto: *Inst. Ven.*, 69, 1382.

### *Cadmium-Tin.*

The equilibrium diagram by Lorentz and Plumbridge [14] shows that the freezing point curve (Fig. 5) consists of two branches meeting at a eutectic when the alloy contains about 28 per cent. cadmium. These alloys are heterogeneous mixtures in all proportions.

FIG. 4.




The electrical conductivity curve by Matthiessen and Vogt [15] is a straight line. The curve giving the thermoelectric power as a function of the concentration is also a straight line. Besides these observations by Rudolfi [12] there are some earlier observations by Battelli.[16] Both of these curves are characteristic of alloys formed by mechanical mixtures of the constituents. Concerning the other

[14] Lorentz and Plumbridge: *Zeit. anorg. Chem.*, 83, 237, 1913.

[15] Matthessien: *Pogg. Ann.*, 110, 206, 1860.

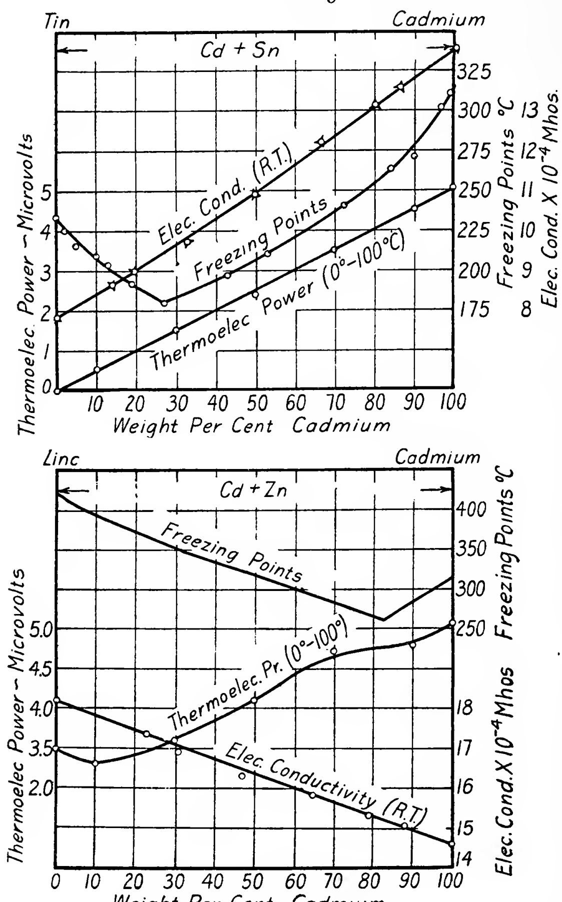
[16] Battelli: *Mem. di Torino* (2), 36, 31, 1884.

thermal, electrical and magnetic properties of these alloys, no observations seem to be available.

*Cadmium-Zinc.*

The freezing point curve for cadmium-zinc alloys by Lorentz and Plumbridge [17] (Fig. 5) consists of two branches meeting at the

FIG. 5.




eutectic for which the temperature is 270° C. The alloys are mechanical mixtures of zinc and cadmium.

[17] Lorentz and Plumbridge: *Zeit. anorg. Chem.*, **83**, 236, 1913.

The electrical conductivities at room temperature have been measured by Matthiessen [18] and also by Vincentini. The curve showing the electrical conductivity as a function of the concentration of one of the constituents come out to be a straight line, as it should for this type of alloys. Battelli [19] has made a study of the thermoelectromotive forces of these alloys and a later investigation was made by Rudolfi.[20] The average values of the thermoelectric powers as determined by Rudolfi have been plotted on the curve in Fig. 5. This curve departs somewhat from a straight line and suggests by its minimum for low concentrations of cadmium that cadmium may be soluble to a limited extent in zinc.

### *Aluminium-Tin.*

The freezing point curves of Gautier [21] and Gwyer [22] for this series of alloys differ by the fact that the freezing point curve of Gautier has a maximum corresponding to the compound AlSn and the curve by Gwyer shows no such maximum. The curve by Gwyer seems to be preferred and it has been reproduced in Fig. 6. According to Gwyer, there seems to be a eutectic which coincides nearly with the melting point of tin. Except for the possibility of slight solubility in each other these metals form alloys which are mechanical mixtures.

Besides the observations of Broniewski [23] on the electrical properties of these alloys there are available some observations by Pecheux on their thermoelectromotive force. The data given by Broniewski have been used for the curves plotted in Fig. 6. These curves in agreement with the freezing point curve lead to the conclusion that these metals do not form definite compounds and are characterized by dilute solid solution of tin in aluminium and a mixture of this solution with tin.

### *Aluminium-Bismuth.*

Gwyer [24] found by thermal analysis that the solubility of aluminium in bismuth is about 2 per cent. and that of bismuth in

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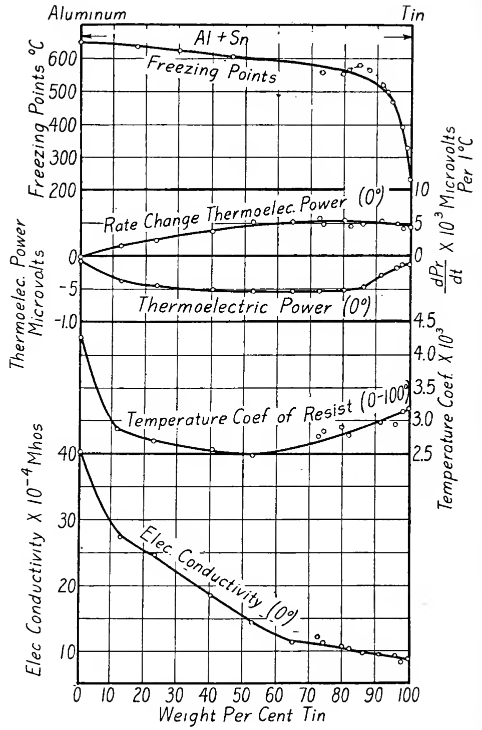
[18] Matthiessen: *Pogg. Ann.*, **110**, 28, 1860.
[19] Battelli: *Atti. R. Inst. Veneto* (6) **5**, 1148, 1886.
[20] Rudolfi: *Zeit. anorg. Chem.*, **67**, 65, 1910.
[21] Gautier: *C. R.*, **123**, 109, 1896.
[22] Gwyer: *Zeit. anorg. Chem.*, **49**, 315, 1906.
[23] Broniewski: *Ann. de Phys. et Chem.* (8) **25**, 63, 1912.
[24] Gwyer: *Zeit. anorg. Chem.*, **49**, 316, 1906.

aluminium is about 4 per cent. at 650° C., but inappreciable at the melting point of bismuth. The alloys may, therefore, be regarded as mechanical mixtures of aluminium and bismuth. The freezing point curve of Fig. 7 is by Gwyer.

Some work has been done by Pecheux [25] on the thermoelectromotive forces in these alloys. They were more fully studied by

FIG. 6.



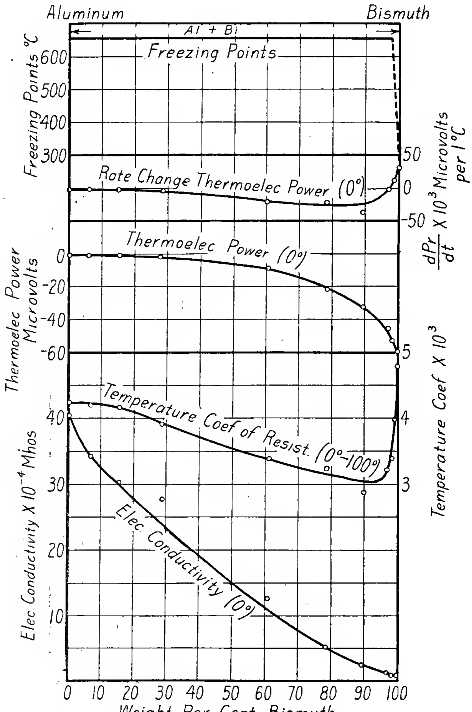

Broniewski [26] from whose observations the curves in Fig. 7 have been taken. Except for a slight minimum where the concentration of aluminium is small the curve for electrical conductivities is nearly a straight line, as it should be for alloys formed by metals which are mechanically mixed. The curve for the temperature

[25] Pecheux: *C. R.*, **138**, 1501, 1904.

[26] Broniewski: *Ann. de Phys. et Chem.* (8), **25**, 66, 1912.

coefficient of the resistance has a minimum at about 95 per cent. bismuth. This together with the slight minimum in the electrical conductivity curve indicates the formation of a solid solution of aluminium in bismuth. Since these minima are more pronounced

FIG. 7.




in the unannealed than in the annealed specimens the solid solution is probably decomposed by annealing.

## METALS COMPLETELY SOLUBLE IN EACH OTHER.

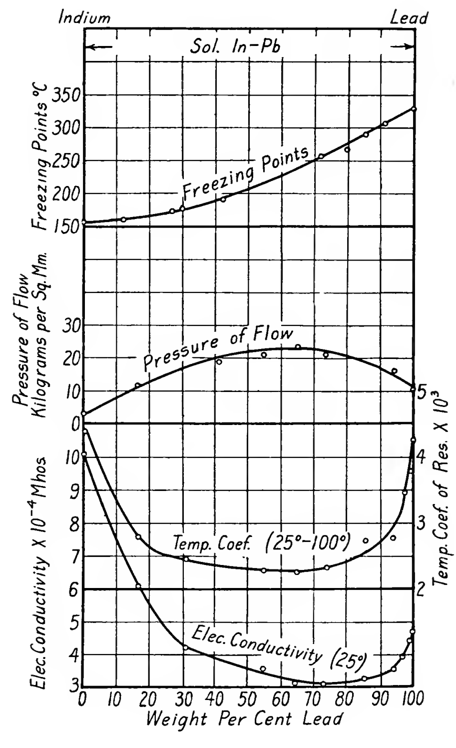
### *Indium-Lead.*

Lead and indium form an isomorphous mixture in all proportions. The freezing point curve (Fig. 8) by Kurnakow and Puschin [27] is a continuous curve through the melting points of lead and indium.

[27] Kurnakow and Puschin: *Zeit. anorg. Chem.*, **52**, 430, 1907.

The electrical conductivity and the temperature coefficient have been measured by Kurnakow and Zemczuzny.[28] These authors have also determined the pressure necessary to cause these alloys to flow. All of the curves representing these physical quantities as

FIG. 8.




functions of the concentration are typical of alloys in which the constituents form a continuous series of mixed crystals. The pressure necessary to produce flow has a maximum value where the electrical conductivity and the temperature coefficient of the resistance have minimum values. This indicates that the electrical properties are in part at least determined by the elastic properties.

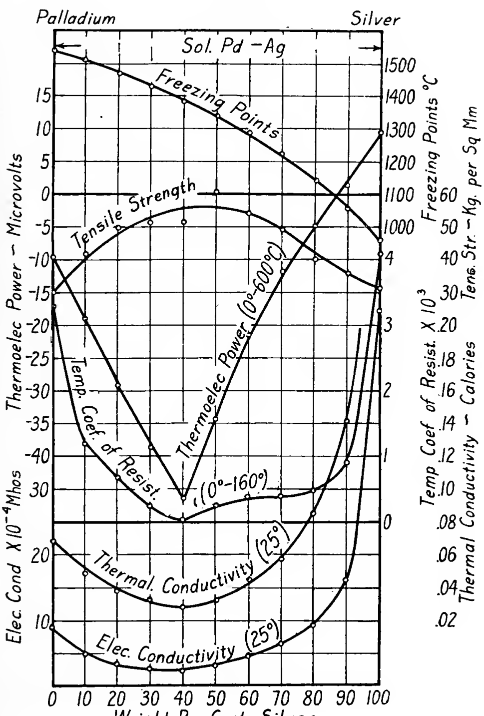
[28] Kurnakow and Zemczuzny: *Zeit. anorg. Chem.*, 64, 149, 1909.

*Palladium-Silver.*

The freezing point curve of these alloys (Fig. 9) is plotted from the data of Ruer.[29] The metals form solid solutions in all proportions.

The electrical and thermal conductivities have been determined by Schulze.[30] He used the same specimens which had been used by Giebel [31] for the study of the electrical conductivity, the tem-

FIG. 9.




perature coefficient of the resistance, the thermoelectric heights and the tensile strength. All of these curves except possibly the one for thermoelectric heights are characteristic of metals which

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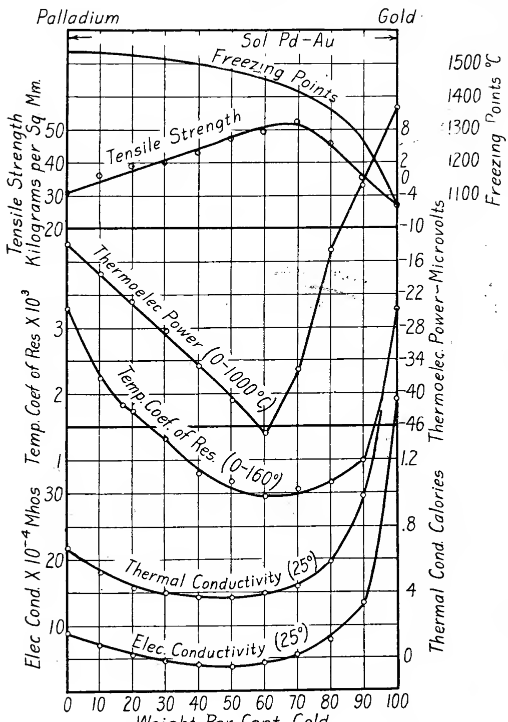
[29] Ruer: *Zeit. anorg. Chem.*, **51**, 315, 1906.
[30] Schulze: *Physikal Zeitschr.*, **12**, 1029, 1911.
[31] Giebel: *Zeit. anorg. Chem.*, **70**, 240, 1911.

form a continuous series of mixed crystals. The elastic properties as represented by the tensible strength of these alloys have a maximum where the electrical conductivity, the thermal conductivity, the thermoelectric power and the temperature coefficient of the resistance have minimum values.

FIG. 10.




*Palladium-Gold.*

From the freezing point curve of Ruer [2] (Fig. 10) it is seen that the freezing point of these alloys changes gradually from the melting point of palladium to the melting point of gold. The metals form an unbroken series of mixed crystals.

The electrical and thermal conductivities have been measured by Schulze [3] and the thermoelectric powers, the temperature coefficient and the tensile strengths by Giebel [32] who also measured the

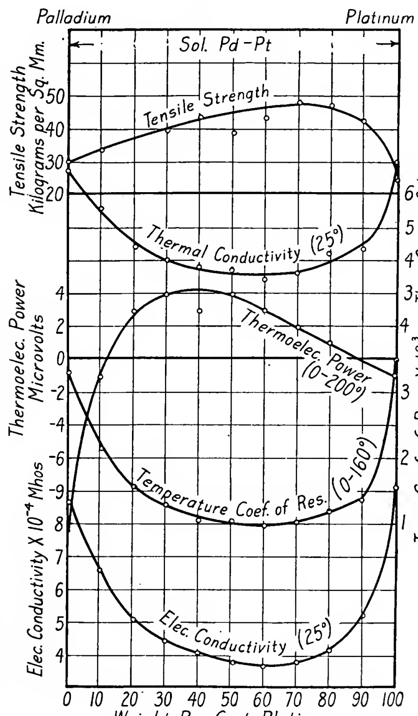
[32] Giebel: *Zeit. anorg. Chem.*, 70, 240, 1911.

electrical conductivity. All of these observations were made on the same specimens. These curves are all very similar to the corresponding curves for palladium-silver alloys and typical of alloys in which there is an unbroken series of mixed crystals. Here as in other similar cases the elastic properties are related to the electrical and thermal properties.

*Palladium-Platinum.*

The freezing point curve for this series of alloys does not seem to have been studied. The physical properties (Fig. 11) clearly

FIG. 11.

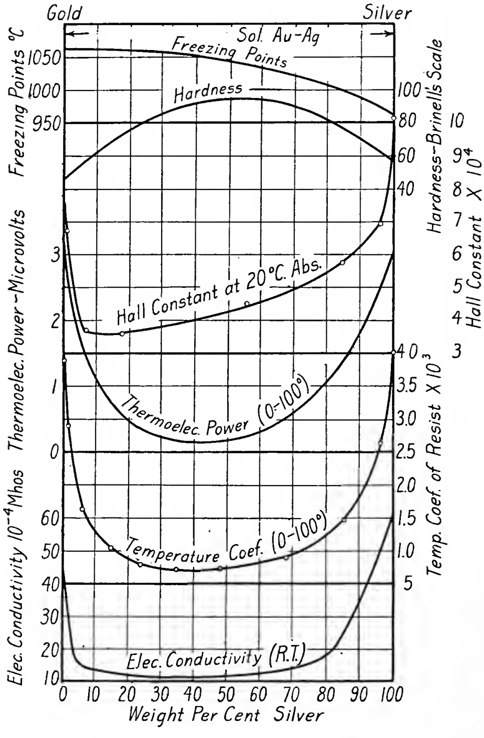



indicate that these metals mix in all proportions forming a continuous series of mixed crystals.

The thermal and electrical conductivities which have been given in Fig. 11 have been taken from the work of Schulze who made

his observations on the same specimens on which Giebel [32] had made observations on the electrical conductivity, the temperature coefficient of the resistance, the thermoelectric power and the tensile strength. There is an evident parallelism between the elec-

FIG. 12.




trical and thermal conductivities. In this series as in the palladium-silver series the curve of tensile strengths has a maximum where the electrical and thermal conductivities have minimum values.

## *Gold-Silver.*

Roberts-Austen and Kirke Rose, confirming the work of Heycock and Neville,[33] showed that gold and silver solidify in the form of an unbroken series of mixed crystals. The freezing point changes continuously from its value in gold to its value in silver.

[33] Heycock and Neville: *Phil. Trans. A.*, 189, A, 69, 1897.

The curve for the electrical conductivities (Fig. 12) is plotted from the observations of Matthiessen.[34] The average thermoelectric power has been calculated from the data of Rudolfi [35] and the Hall constant from the work of Beckman.[36] The hardness has been measured by Kurnakow.[37] The similarity between the four lower curves in Fig. 12 is very evident. The elastic property has a maximum value where the other properties have minimum values, indicating that the elastic forces in the alloys help to determine the Hall effect as well as the electrical conductivity, the temperature coefficient of the resistance and the thermoelectric powers.

### *Copper-Gold.*

From the observations of Kurnakow and Zemczuzny [38] on the freezing points of copper-gold alloys (Fig. 13) it is found that the freezing point curve runs in a simple way from the melting point of copper to the melting point of gold. It has a minimum where the alloy contains about 25 per cent. copper. These metals form a continuous series of solid solutions.

The electrical conductivity of this series has been studied by Matthiessen [39] and in later times by Kurnakow, Zemczuzny and Zasedatelev [40] from whose observations have been taken both the curve for electrical conductivities and the curve for temperature coefficient of resistance. The hardness which has been measured by Kurnakow and Zemczuzny [41] shows the maximum which is characteristic of a series of solid solutions. The average thermoelectric power as found by Rudolfi [1] has been used for the thermoelectric height curve. Except for the two peaks in the curve for the electrical conductivity and two corresponding peaks in the curve for the temperature coefficient of the resistance, this set of curves is very similar to the set found for alloys of platinum and palladium in which there was a continuous series of solid solutions.

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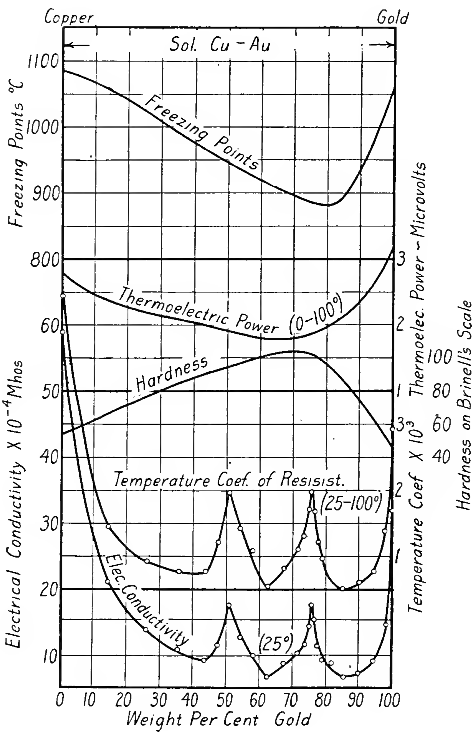
[34] Matthiessen: *Pogg. Ann.*, **110**, 190, 1861.
[35] Rudolfi: *Zeit. anorg. Chem.*, **67**, 65, 1910.
[36] Beckman: *Com. fr. Phys. Lab. Univ. of Leiden*, **130**, 27, 1912.
[37] Kurnakow: *Zeit. anorg. Chem.*, **60**, 1, 1908.
[38] Kurnakow and Zemczuzny: *Zeit. anorg. Chem.*, **54**, 163, 1907.
[39] Matthiessen: *Pogg. Ann.*, **110**, 217, 1860.
[40] Kurnakow, Zemczuzny and Zasedatelev: *J. Inst. of Metals*, **15**, 305, 1916.
[41] Kurnakow and Zemczuzny: *Zeit. anorg. Chem.*, **60**, 1, 1908.

*Potassium-Rubidium.*

These metals form isomorphous mixtures in all proportions. The freezing point curve has not been located and it seems to be unknown.

The observations on the electrical conductivity and on the rate of change of the resistance with the temperature (Fig. 14) are

FIG. 13.

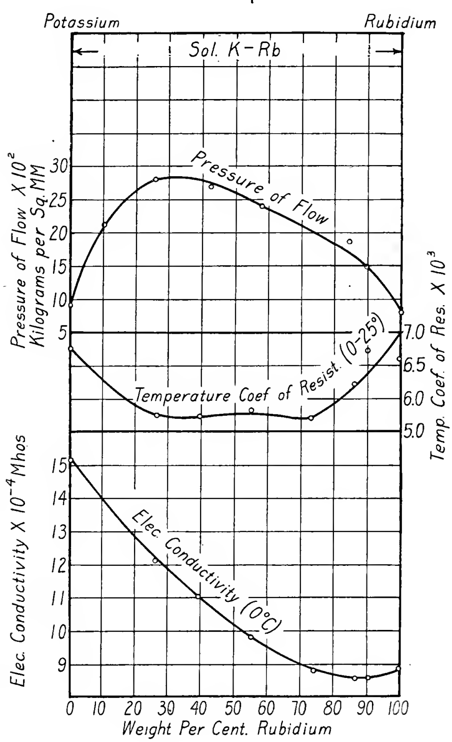



due to Kurnakow and Nikitinsky.[42] They also determined the pressures required to cause the alloys to flow. The electrical conductivity as a function of the concentration of one of the components is represented by a continuous curve with a very slight minimum. This is characteristic of isomorphous mixtures. With rising temperature the minimum is displaced toward rubidium—

[42] Kurnakow and Nikitinsky: *Zeit. anorg. Chem.*, **88**, 151, 1914.

the metal with the least conductivity. The curve for the rate of change of the resistance with the temperature shows the minimum characteristic of this type of alloys. The only difference between these curves and those obtained under similar conditions for most isomorphous mixtures is the smaller decrease in the electrical conductivity which is produced by adding rubidium to potassium. In most cases in which solid solutions are formed this decrease is

FIG. 14.



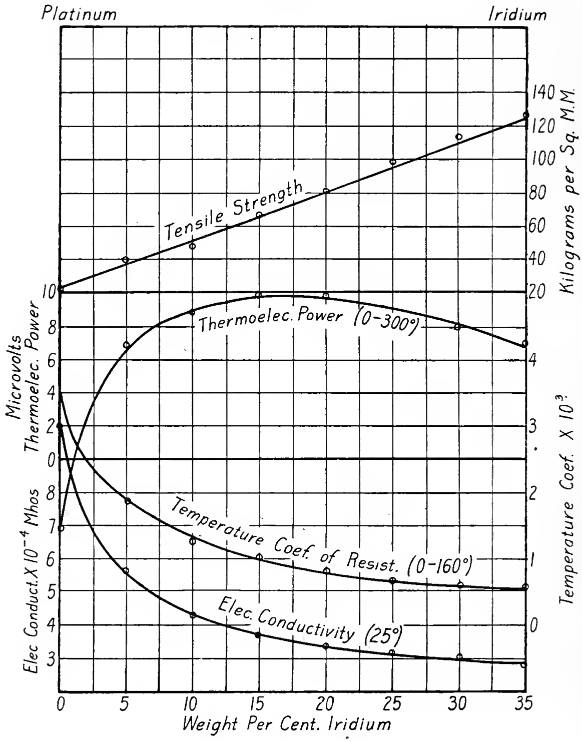

much larger than it is in this case. The elastic properties as measured by the pressure necessary to cause the alloys to flow show the characteristic maximum found in isomorphous mixtures.

## *Platinum-Iridium.*

The equilibrium diagram for this series has not been located. These metals probably form solid solutions.

The electrical conductivity, the temperature coefficient, the thermoelectric power, and the tensile strength have been studied by Giebel[43] for this series of alloys for concentrations of iridium between 0 and 35 per cent. These curves are reproduced in Fig. 15. The tensile strength is a linear function of the concentration of iridium over this interval. The thermoelectric power passes through a maximum between 15 and 20 per cent. iridium. The addition of iridium to platinum lowers both the electrical conductivity and the temperature coefficient in the way to be expected on the assumption that the metals form solid solutions.

FIG. 15.



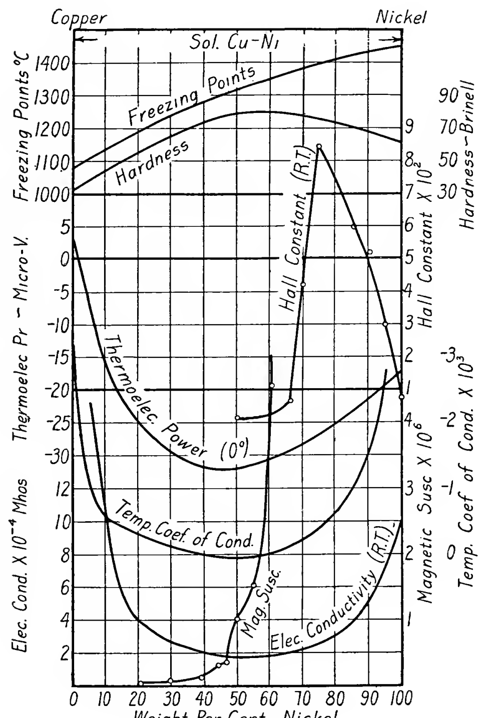

[43] Giebel: *Zeit. anorg. Chem.*, 70, 247, 1911.

*Copper-Nickel.*

The freezing point curve for this series of alloys (Fig. 16) is the one worked out by Guertler and Tammann.[44] These metals form an unbroken series of solid solutions.

The electrical conductivity and the temperature coefficient have

FIG. 16.




been measured by Feussner.[45] The curves thus obtained are characteristic of a continuous series of solid solutions. The thermoelectric power by Englisch[46] and the hardness by Kurnakow and Papke[47] also give the type of curve to be expected in alloys which

[44] Guertler and Tammann: *Zeit. anorg. Chem.*, 53, 281, 1907.
[45] Feussner: *Verhand. d. physik Gesel. zu Berlin*, 10, 109, 1891.
[46] Englisch: *Phys. Consts. Soc. Fran. de Phys.*, p. 654, 1893.
[47] Kurnakow and Papke: *Zeit. anorg. Chem.*, 87, 274, 1914.

are solid solutions. The curve of hardness shows a maximum where the curve for the electrical conductivity has a minimum, thus showing that the elastic properties in a measure determine the electrical conductivity and its variation with the temperature. The curve for the magnetic susceptibilities has been taken from the observations of Gans and Fouseca.[48] The Hall constant is by the author.[49] Neither the Hall constants nor the magnetic susceptibilities seem to depend on the concentration in the way to be expected for solid solutions.

### *Iron-Nickel.*

The freezing point curve (Fig. 17) by Guertler and Tammann [50] indicates that iron and nickel form a continuous series of solid solutions. On the freezing point curve as sometimes given there seems to be a change in curvature at the concentration corresponding to the compound $Ni_2Fe$, from which this compound is sometimes inferred.

The specific heat, the electrical conductivity, the temperature coefficient, the thermal conductivity and the thermoelectric heights have been measured by Ingersoll and others.[51] The flux densities given in Fig. 17 are from the observations of Yensen [52] and were measured for an external magnetic field of 400 gausses. The specific heat is a maximum at the concentration of the possible compound $Ni_2Fe$. The electrical conductivity, the temperature coefficient and the thermoelectric power have minimum values where the intermetallic compound might be formed. Of all these curves only the one for the thermal conductivities has the general form to be expected in a series of alloys which are an unbroken series of solid solutions. The complexity of the curves in this case is doubtless due to the fact that both nickel and iron are polymorphic.

### *Magnesium-Cadmium.*

The freezing point curve by Grube [53] has a point of inflection where the concentration corresponds to the compound MgCd.

[48] Gans and Fouseca: *Ann. d. Phys.*, 61, 742, 1920.

[49] Smith: *Phys. Rev., N. S.*, 17, 24, 1921.

[50] Guertler and Tammann: *Zeit. anorg. Chem.*, 45, 205, 1905.

[51] Ingersoll: *Phys. Rev., N. S.*, 16, 85, 1920.

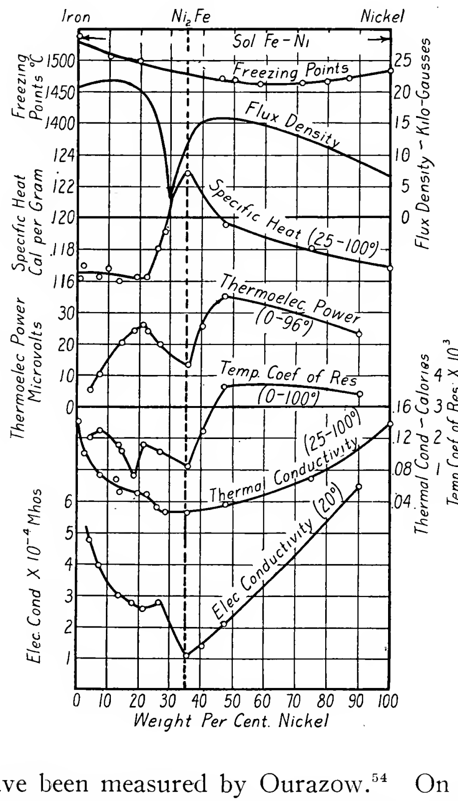
[52] Yensen: *Jour. A. I. E. E.*, 396, 1920.

[53] Grube: *Zeit. anorg. Chem.*, 49, 72, 1906.

This change in curvature is not very evident in the curve as plotted in Fig. 18. According to this equilibrium diagram the alloys are solid solutions of two crystalline phases. About the equilibrium in this series there is still considerable doubt.

The electrical conductivity, the temperature coefficient, and

FIG. 17.

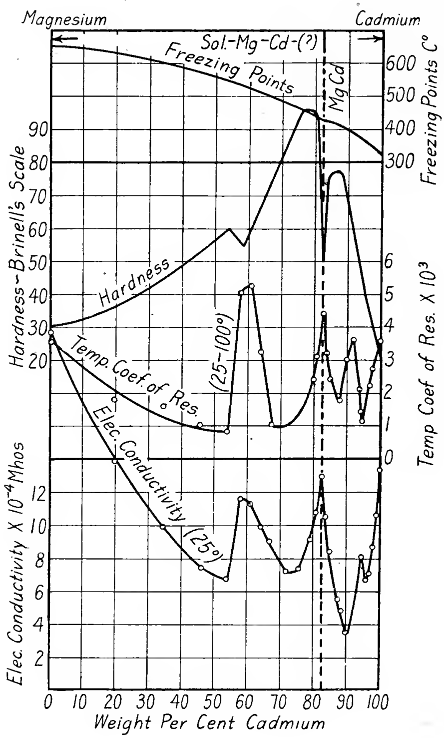



hardness have been measured by Ourazow.[54] On both of these curves the compound MgCd is clearly marked by a cusp. This compound is also indicated on the curve for hardness. On either side of the compound there is a second cusp in the curve for electrical conductivity and for the temperature coefficient. If these cusps were absent the curves would have the normal course

[54] Ourazow: *Zeit. anorg. Chem.*, 73, 31, 1912.

to be expected on the assumption that alloys to the right of the compound are solid solutions of cadmium and the compound MgCd and those to the left of the compound solid solutions of magnesium with the compound MgCd. The thermal analysis is

FIG. 18.




not in agreement with the indications given by the thermal and electrical properties in this case.

### METALS WITH LIMITED SOLUBILITY IN EACH OTHER.

#### *Aluminium-Zinc.*

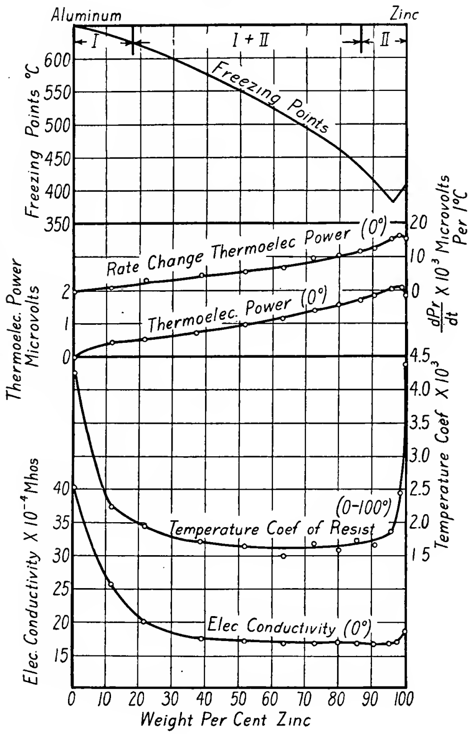
The freezing point curve of aluminium-zinc alloys from Gautier[55] (Fig. 19) is made up of two branches which meet at the temperature of fusion of the eutectic. There are no compounds

[55] Gautier: *Bull. Soc. Encour.* (5), 1, 1293, 1896.

and Shepherd [56] concludes from a micrographic study that aluminium-zinc alloys are formed of two solid solutions and a mechanical mixture of these solid solutions.

Besides the observations of Broniewski [57] on the electrical

FIG. 19.




properties of these alloys there are earlier observations by Battelli [58] and Pecheux.[59] The curves in Fig. 19 have been plotted from the observations of Broniewski. The curves all belong to that group of alloys which are formed from metals which are soluble in each other to a limited extent and in which the solid solutions

[56] Shepherd: *Jour. Phys. Chem.*, 9, 504, 1905.

[57] Broniewski: *Ann. de Chem. et Phys.* (8), 25, 1, 1912.

[58] Battelli: *Atti. R. Inst. Veneto.* (6), 5, 1148, 1886-7.

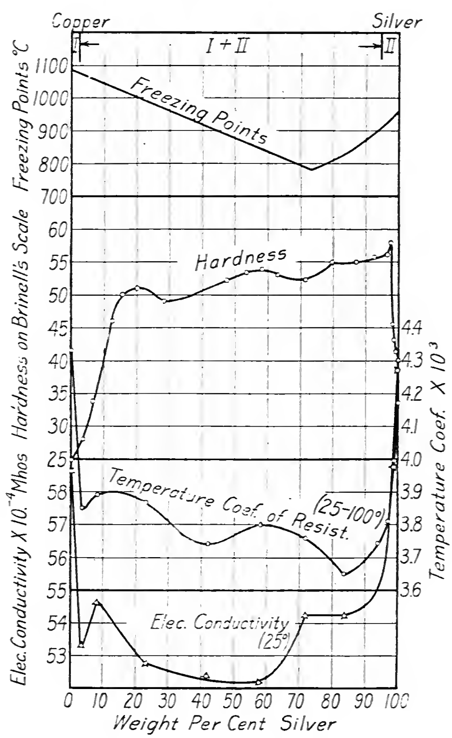
[59] Pecheux: *C. R.*, 138, 1103, 1904.

thus formed mix with each other mechanically. The central portions of the curves are nearly linear as should be the case for mechanical mixtures.

## *Copper-Silver.*

A thermal analysis of copper-silver alloys has been made by Heycock and Neville.[60] Their results have been confirmed by the

FIG. 20.




work of Friedrick and Leroux and Lepowiski,[61] from whose work the freezing point curve (Fig. 20) is taken. Copper forms a solid solution with silver and silver with copper until the concentration of the copper in one case and silver in the other is about

[60] Heycock and Neville: *Phil. Trans. A.*, 189, 25, 1897.

[61] Lepowiski: *Zeit. anorg. Chem.*, 59, 289, 1908.

5 per cent. The remainder of the alloys are heterogeneous mixtures of these saturated solid solutions.

The hardness, the electrical conductivity and the temperature coefficient of this series are due to Kurnakow, Puschin and Semkowsky.[62] Where a solid solution is formed between copper and silver there is a marked lowering of both the electrical conductivity and the temperature coefficient. Hence for high as well as low concentrations of silver these curves are very steep. The central portions of these curves, although somewhat irregular, approach the form to be expected in a region where there is a mechanical mixture of two crystalline phases. There is a marked increase in hardness over the intervals in which solid solutions are formed. The remainder of the hardness curve is such as is to be found where the alloys are mechanical mixtures of two crystalline phases. Except for some irregularities this set of curves clearly belongs to metals which form solid solutions with each other to a limited extent and then these solid solutions mix mechanically to form the remainder of the alloys.

### *Bismuth-Lead.*

The freezing point curve by Kapp and Charpy [63] (Fig. 21) has a eutectic at 56.5 per cent. bismuth. Herold [64] finds that for suitable concentrations lead and bismuth form mixed crystals, but the region over which these solid solutions extend is not clearly defined. The solutions, however, are rather dilute. The remainder of the alloys are mechanical mixtures of two crystalline phases.

The hardness curve indicates by the increase in hardness for low and high concentrations of bismuth the formation of solid solutions at the beginning and end of this series. The remainder of the curve of hardness over the region where the alloys are heterogeneous mixtures is a straight line. The thermal and electrical conductivities by Schulze [65] have minima for alloys containing 4 or 5 per cent. of lead. This as well as the initial drops in these curves for alloys containing from 0 to 15 per cent. bismuth is further evidence for the formation of solid solutions at either end of this series. The thermoelectromotive force which

[62] Kurnakow, Puschin and Semkowsky: *J. d. russ. phys. Chem.*, **42**, 733, 1910.

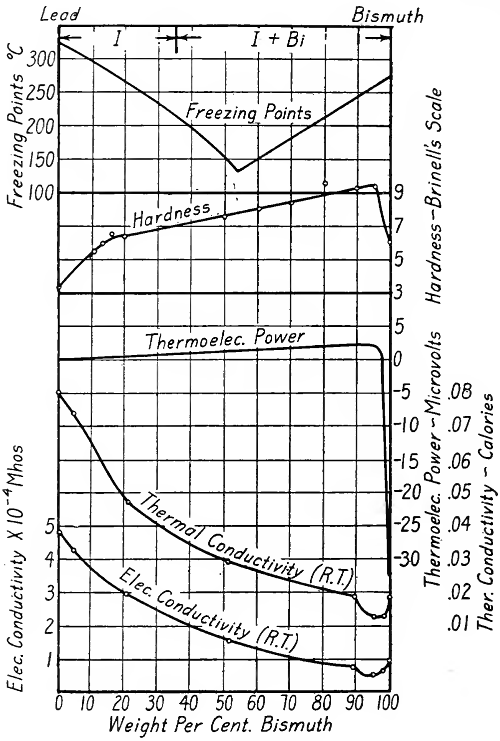
[63] Barlow: *Zeit. anorg. Chem.*, **70**, 183, 1911.

[64] Herold: *Zeit. anorg. Chem.*, **112**, 131, 1920.

[65] Schulze: *Ann. d. Phys.*, **9**, 564, 1902.

has been studied by Battelli [66] shows a rapid decrease for the addition of small quantities of lead to bismuth. The characteristics of this curve in this region are similar to the characteristics of the other curves over this same region.

FIG. 21.




## *Antimony-Tin.*

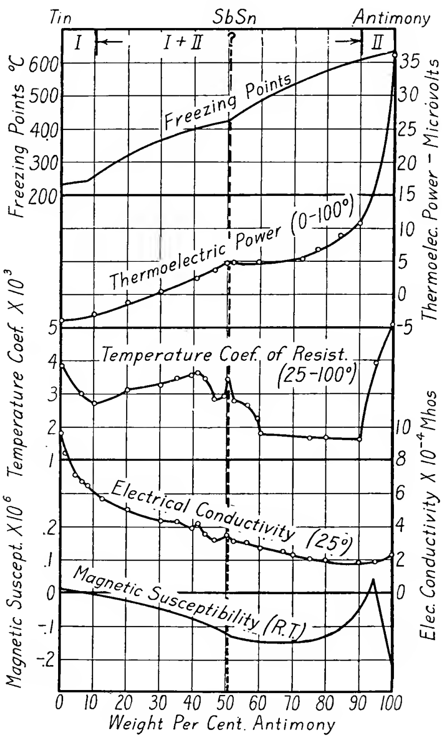
The freezing point curve by Williams [67] (Fig. 22) consists of three parts. Later study of equilibrium in this system has been made by Konstantinow and Smirnow, LeGris and Loebe. Between 90 and 100 per cent. antimony there is a solid solution of tin in antimony and between 0 and 10 per cent. tin there is a

[66] Battelli: *Atti. R. Inst. Veneto* (6), 5, 1148, 1886.
[67] Williams: *Zeit. anorg. Chem.*, 55, 12, 1907.

solid solution of antimony in tin. When the metals are present in equal concentrations a new crystalline phase is formed, probably the intermetallic compound SnSb. Those alloys which are not solid solutions for large and small concentrations of antimony are mechanical mixtures of two crystalline phases.

The electrical conductivity and the temperature coefficient are

FIG. 22.




by Konstantinow and Smirnow [68] and the magnetic susceptibility by Leroux.[69] The initial decrease in the electrical conductivity, the temperature coefficient of the resistance and the thermoelectric power [70] caused by the addition of tin to antimony give evidence

[68] "Annual Tables of Constants and Numerical Data," Vol. 2, p. 345.

[69] Leroux: *C. R.*, **156**, 1764, 1913.

[70] Hutchins: *Jour. Am., Amer. Jour. Sci.*, **48**, p. 226, 1894.

of the formation of a solid solution over this region. On the other side of the diagram where the concentration of antimony is less than 10 per cent. the curve for the electrical conductivity and for the temperature coefficient show again the presence of solid solutions. The curve for the magnetic susceptibilities indicates the compound by a change in its curvature at that concentration. The evidence for the structure of this series is not conclusive.

### *Lead-Thallium.*

The freezing point curve for lead-thallium alloys has a very flat maximum between 30 and 40 per cent. lead. This was regarded by Lewkonja[71] as evidence of the compound $PbTh_2$. Kurnakow and Puschin[72] found that this maximum is displaced by the addition of tin to the alloys. If the maximum were due to a true compound, this displacement should not occur. Hence the existence of the compound is in doubt. Thallium forms a solid solution with lead until the concentration of thallium is about 75 per cent., and lead dissolves in thallium until the concentration of lead is about 4 or 5 per cent. Rejecting the evidence for the existence of the compound, the alloys between 5 and 25 per cent. lead are heterogeneous mixtures of a saturated solution of lead in thallium with a saturated solution of thallium in lead.

The electrical conductivity and the mean temperature coefficient as determined by Kurnakow and Schemtschuschny[73] have been plotted in Fig. 23. There is a minimum in both curves. This minimum is in the region over which lead and thallium form an isomorphous mixture. The addition of lead to thallium causes a decrease in the electrical conductivity and also in the temperature coefficient of the resistance. This decrease is followed by an increase which extends to the concentration at which the solution is saturated with lead. Between 5 and 25 per cent. lead there is a straight line portion in the curve. This is over the region where the alloys are mechanical mixtures of two crystalline phases. The pressure required to produce flow in these alloys is taken from these same observers. The curve thus obtained shows the characteristic relation between the electrical and the elastic properties.

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[71] Lewkonja: *Zeit. anorg. Chem.*, 52, 452, 1907.

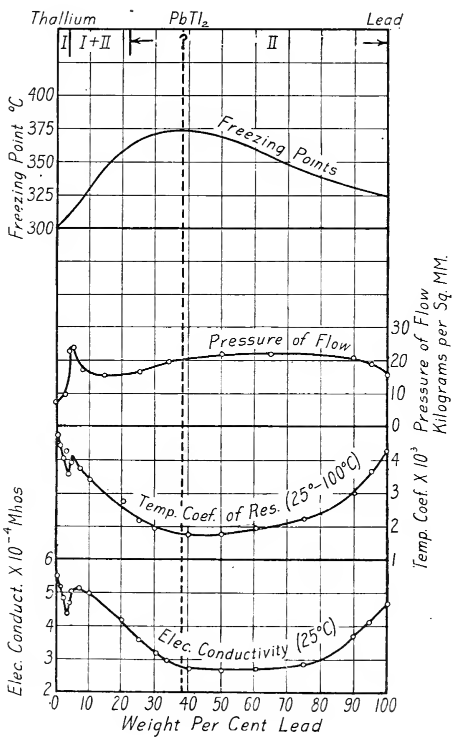
[72] Kurnakow and Puschin: *Zeit. anorg. Chem.*, 52, 430, 1907.

[73] Kurnakow and Schemtschuschny: *Zeit. anorg. Chem.*, 64, 156, 1909.

*Lead-Antimony.*

The freezing point curve (Fig. 24) by Gontermann [74] shows a eutectic in the neighborhood of 13 per cent. antimony. Gontermann finds some evidence of an intermediate crystalline constituent. Aside from this possible exception these alloys may be considered mechanical mixtures.

FIG. 23.




The curve for electrical conductivities is by Matthiessen; [75] for the thermoelectric powers by Rudolfi; [76] for magnetic susceptibilities by Leroux, [77] and for the electromotive force of dissolution by Pouchine. The curve for the thermoelectric powers is a straight

[74] Gontermann: *Zeit. anorg. Chem.*, **55**, 419, 1907.

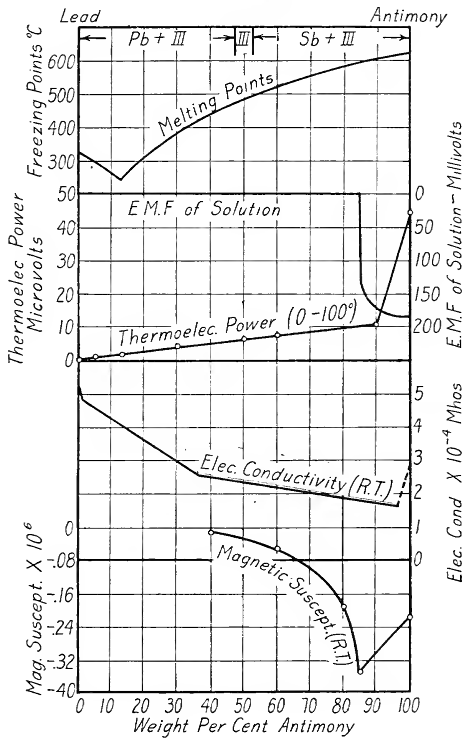
[75] Matthiessen: *Pogg. Ann.*, 110, 28, 1860.

[76] Rudolfi: *Zeit. anorg. Chem.*, 67, 65, 1910.

[77] Leroux: *C. R.*, 156, 1764, 1913.

line until the alloy contains 90 per cent. antimony. At that concentration the thermoelectric power rises rapidly to its value in pure antimony. At about this same concentration the curve for the magnetic susceptibilities and for the electromotive forces of solution show peculiarities. There seems to be nothing in the struc-

FIG. 24.




ture of the alloys to offer an explanation of this sudden change in the direction of the curves at this concentration.

## *Copper-Cobalt.*

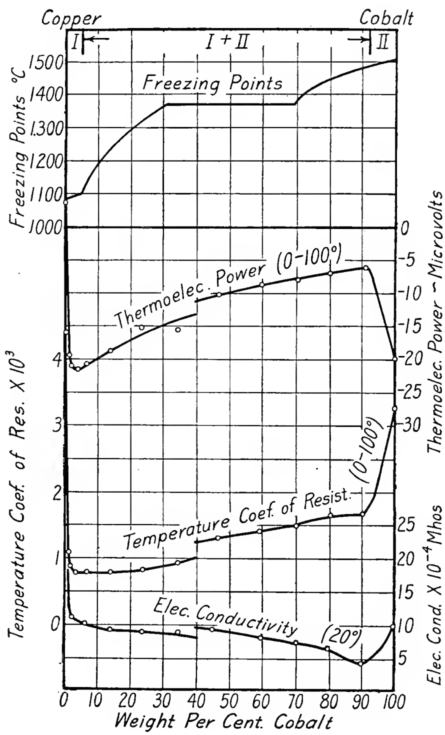
The equilibrium diagram by Sahmen[78] from which the freezing point curve (Fig. 25) is taken shows that copper and cobalt form mixed crystals with each other over a limited region. Cop-

[78] Sahmen: *Zeit. anora Chem.*, 57, 1908.

per is soluble in cobalt up to 8 per cent. and cobalt in copper up to 5 per cent. cobalt. The remainder of the alloys are a heterogeneous mixture of a saturated solution of cobalt in copper and a saturated solution of copper in cobalt.

The curve for electrical conductivity, temperature coefficient and thermoelectric height are from the observations of Reichardt.[79]

FIG. 25.

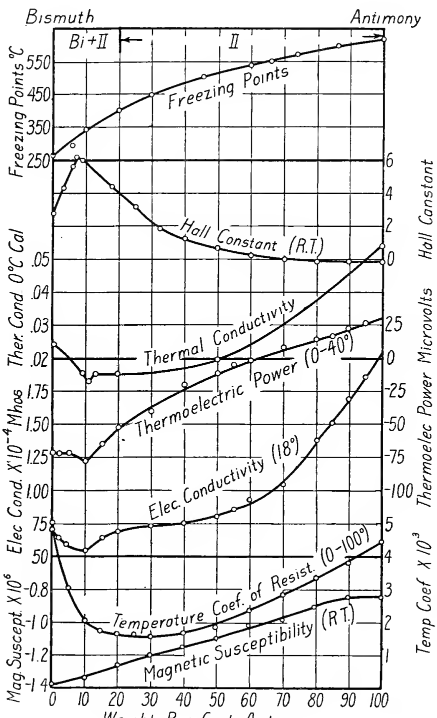



Each of these curves shows a discontinuity since alloys with less than 60 per cent. copper were so brittle that they could not be forged into wires and were investigated in the form of castings. Aside from these discontinuities the curve for electrical conductivity and the curve for temperature coefficient of resistance are typical of alloys in which the constituents are soluble in each other

[79] Reichardt: *Ann. d. Phys.*, 6, 842, 1901.

to a limited extent. The central portion of the curves are essentially linear, as they should be for alloys formed by the mixture of two crystalline phases. The curve for thermoelectric powers is peculiar in view of the fact that the addition of cobalt to copper causes a rapid decrease in the thermoelectric height and the addition of copper to cobalt causes a somewhat less rapid increase in the thermoelectric height of cobalt.

FIG. 26.




## *Bismuth-Antimony.*

The freezing point curve (Fig. 26) by Huttner and Tammann [80] shows that the freezing points of these alloys decrease gradually from the melting point of bismuth. Concerning the structure of the alloys there seems to be some doubt. Between 18

[80] Huttner and Tammann: *Zeit. anorg. Chem.*, **44**, 131, 1905.

and 100 per cent. antimony they may be considered solid solutions of bismuth and antimony and between 0 and 18 per cent. antimony they are mixtures of bismuth and a saturated solution of antimony and bismuth.

The thermoelectromotive forces of this series have been studied by Seebeck, Rollmann, Matthiessen, Becquerel, Sundell, Battelli, Hutchins and more recently by Haken [81] from whose data the curve of Fig. 26 is taken. The electrical conductivity is known from the work of Matthiessen, Calvert and Johnason and Haken.[81] The magnetic susceptibility by Honda and Sone [82] is a linear function of the concentration until the alloy contains about 90 per cent. antimony where the proportionality fails. The curve for the thermal conductivities by Gehlhoff and Neumaier [83] is very similar to the curve for electrical conductivities by Haken. This shows that Wiedmann and Franz's law holds approximately for these alloys. The curve for the temperature coefficient is characteristic of alloys which are solid solutions. The Hall constant [84] is evidently closely related to the thermoelectric power in agreement with the suggestion of Beattie that there is a proportionality between these two quantities.

### *Bismuth-Tin.*

The freezing point curve (Fig. 27) from data of Stoffel [85] and Lepkowski [86] consists of two branches meeting at a eutectic. Except for small and possibly large concentrations of tin where the metals may be soluble in each other to a limited extent, these alloys are mechanical mixtures of bismuth and tin.

The thermoelectric powers of these alloys have been studied by Hutchins [87] and also by Caswell.[88] The curve for the Thomson

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[81] Haken: *Ann. d. Phys.*, 32, 291, 1910.

[82] Honda and Sone: *Sci. Repts. Univ. Tokio*, 2, 5, 1913.

[83] Gehlhoff and Neumaier: *Verh. d. Deutsch. Phys. Ges.*, p. 876, 1913.

[84] Smith: *Phys. Rev.*, 32, 178, 1911.

[85] Stoffel: *Zeit. anorg. Chem.*, 53, 148, 1907.

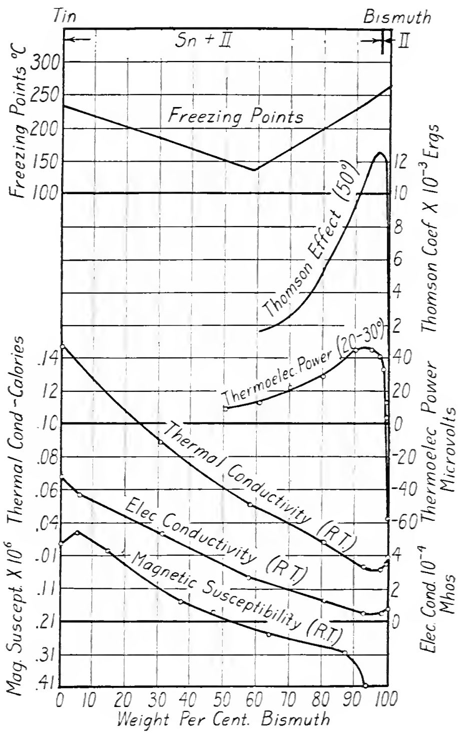
[86] Lepkowski: *Zeit. anorg. Chem.*, 59, 287, 1908.

[87] Hutchins: *Amer. Jour. Sci.*, 48, 226, 1894.

[88] Caswell: *Phys. Rev., N. S.*, 12, 226, 1918.

effect as determined by Laws and also by Caswell is very similar to the curve for the thermoelectric heights. Each curve shows a pronounced maximum when a small quantity of tin is present in the alloy. The curves for electrical and thermal conductivities by Schulze [89] have minima where the preceding curves have maxima.

FIG. 27.




These maxima and minima occur in the region in which the alloys seem to be dilute solid solutions of tin in bismuth. The remainder of the curve for thermal conductivity as well as the curve for electrical conductivity is roughly linear, the form to be expected in alloys which are heterogeneous mixtures. The curve for magnetic susceptibilities has been contributed by Gnesotto and Binghin-

[89] Schulze: *Ann. d. Phys.*, 9, 566, 1902.

notto.[90] The addition of tin to bismuth rapidly decreases the diamagnetic susceptibility in the interval where the preceding curves showed either maxima or minima, that is, in the interval of possible solid solutions. The remainder of the curve suggests mechanical mixtures except for the irregularities where the alloys are nearly all tin.

## *Copper-Zinc.*

The freezing point curve (Fig. 28) is by Shepherd and others.[91] The structure of this series is complex. Copper dissolves zinc until the concentration of zinc is about 35 per cent. and zinc dissolves copper until the concentration of copper is 2 or 3 per cent. The intermediate alloys may be considered heterogeneous mixtures of two crystalline phases.

The electrical conductivity, the temperature coefficient, the thermoelectric powers and the rate of change of thermoelectric power have been measured by Norsa.[92] Between 0 and about 35 per cent. zinc these curves have the form characteristic of alloys which are solid solutions. The remainder of the curves seem too complicated to admit of analysis in terms of the structure of the alloys. The thermal conductivity is known from the work of Calvert and Johnson.[93] The course of this curve is somewhat irregular. The curve for the magnetic susceptibility has been plotted from data by Weber.[94] Between 0 and 35 per cent. zinc it is a straight line.

## *Copper-Tin.*

The structure of this series of alloys is complex. The freezing point curve (Fig. 29) by Heycock and Neville[95] gives evidence of one compound $Cu_3Sn$. Tin is soluble in copper until

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[90] Gnesotto and Binghinnotto: *Inst. Ven.*, 69, 1382.

[91] Guertler: *Metallographie*, i, 459.

[92] Norsa: *C. R.*, **155**, 348, 1912.

[93] Calvert and Johnson: *Phil. Mag.*, **18**, 354, 1850.

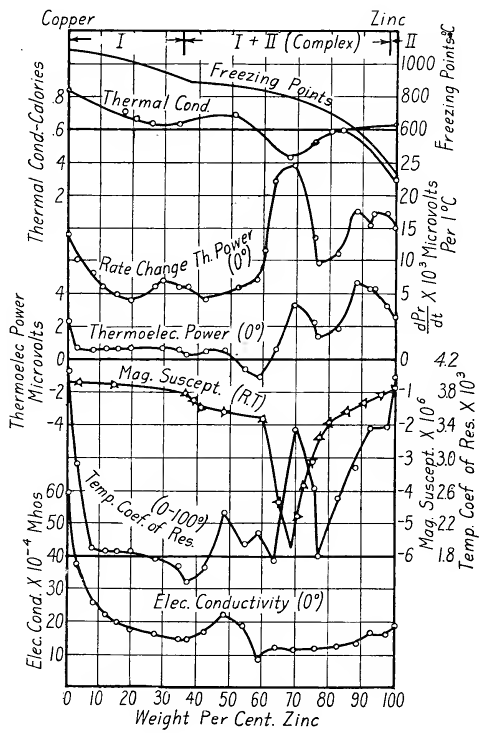
[94] Weber: *Ann. d. Phys.*, **62**, 666, 1920.

[95] Heycock and Neville: *Phil. Trans. A.*, **202**, 1, 1904.

there is about 13 per cent. copper present. The remainder of the alloys may be considered as mechanical mixtures of two crystalline phases.

The curve for hardness by Kurnakow and Zemczuzny [96] consists of two straight lines and a curve of gentle slope. The two

FIG. 28.

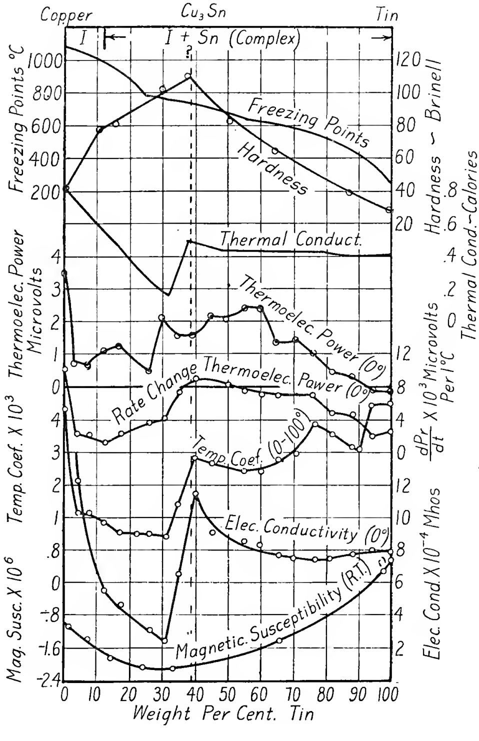



straight lines intersect where the concentration of tin is about 11 per cent. and thus mark the concentration at which tin ceases to be soluble in copper. The intersection of the second straight line with the third portion of the curve marks the concentration for the compound $Cu_3Sn$. The curves for the electrical conductivity, the temperature coefficient, the thermoelectric power and its variation

[96] Kurnakow and Zemczuzny: *Zeit. anorg. Chem.*, 60, 9, 1908.

with the temperature have been plotted from the observations of Leroux.[97] Between 0 and 35 per cent. tin the curves for electrical conductivities and that for the temperature coefficients are typical of alloys which are solid solutions. Where the solution becomes saturated the direction of the curves suddenly changes. The position of the intermetallic compound is marked on these curves

FIG. 29.




by cusps. The curve for thermal conductivities is very similar to the curve for electrical conductivities. Wiedemann and Franz's law must, therefore, hold approximately for these alloys. The curve for the magnetic susceptibilities by Clifford [98] does not show

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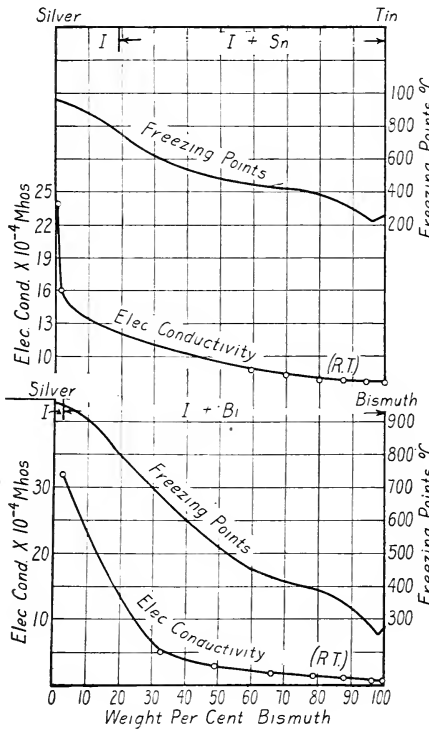
[97] Leroux: *C. R.*, 155, 35, 1912.

[98] Clifford: *Phys. Rev.*, 26, 424, 1908.

the compound, but this is probably due to the fact that the points on the curve near the compound are too far apart.

FIG. 30.




*Silver-Tin.*

The freezing point curve for silver-tin alloys (Fig. 30) by Petrenko [99] is in complete agreement with the curve obtained by Heycock and Neville. Silver is only slightly soluble in tin and tin is soluble in silver until the concentration of tin is about 18 per cent. The other alloys are, therefore, heterogeneous mixtures of two crystalline phases.

The electrical conductivity curve by Matthiessen [100] shows an initial rapid drop for alloys rich in silver. This is characteristic of

[99] Petrenko: *Zeit. anorg. Chem.*, 50, 138, 1906; also 53, 200, 1907.
[100] Matthiessen: *Pogg. Ann.*, 110, 215, 1860.

alloys which are solid solutions. The remainder of the curve has the general shape of curves for a mechanical mixture of two crystalline phases.

*Silver-Bismuth.*

Petrenko [101] has also given the freezing point curve for silver-bismuth alloys (Fig. 30). It shows a eutectic for alloys containing 2.5 per cent. silver. Under suitable conditions bismuth is somewhat soluble in silver. Most of the alloys are heterogeneous mixtures of a saturated solid solution of bismuth in silver and of bismuth.

The form of the electrical conductivity curve by Matthiessen [102] suggests the formation of solid solutions of bismuth in silver followed by a region in which the alloys are heterogeneous mixtures. The electrical conductivity curve for this series is very similar to the curve for silver-tin alloys. Some observations on thermoelectromotive forces have been made by Battelli.[103]

*Lead-Cadmium.*

The freezing point curve, according to Stoffel [104] (Fig. 31), consists of two branches meeting at a eutectic for which the temperature is 249° C. Lead and cadmium form a solid solution until the concentration of cadmium is about 5 per cent., at which concentration the solution is saturated. The remainder of the alloys are a mechanical mixture of this saturated solution and cadmium.

The electrical conductivity by Matthiessen [102] is nearly a linear function of the concentration. There are no points on the curve in the region between 95 and 100 per cent. lead in which the solid solutions are now known to be formed.

*Lead-Silver.*

The freezing point curve by Petrenko [101] (Fig. 31) shows a eutectic for which the temperature is 303.9° C. Lead is soluble in

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[101] Petrenko: *Zeit. anorg. Chem.*, 50, 138, 1906; also 53, 200, 1907.

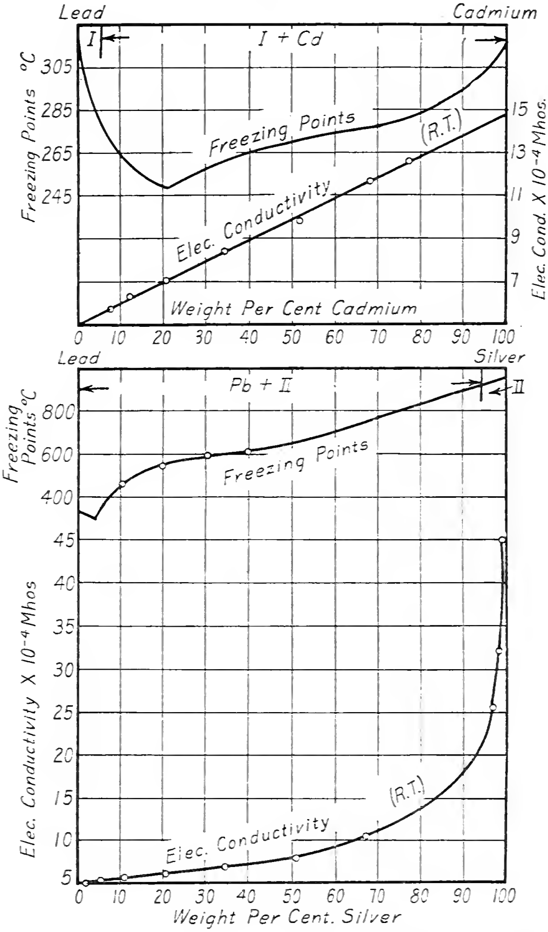
[102] Matthiessen: *Pogg. Ann.*, 110, 208, 1860.

[103] Battelli: *Atti. R. Inst. Ven.* (6), 5, 1148, 1886.

[104] Stoffel: *Zeit. anorg. Chem.*, 53, 152, 1907.

silver until the alloy contains about 5 per cent. lead. The remainder of the alloys are heterogeneous mixtures of this solid

FIG. 31.



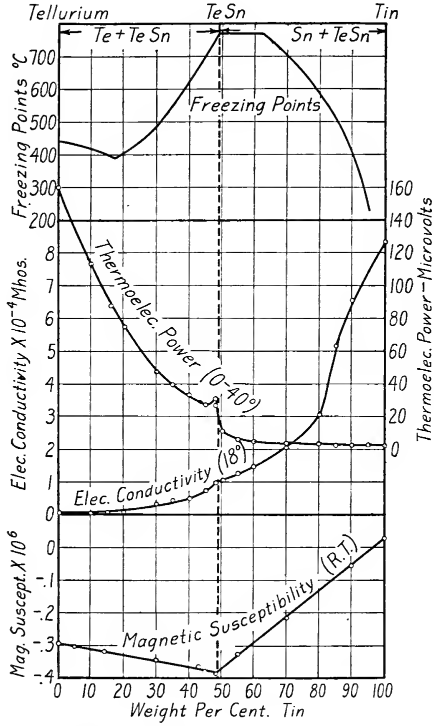

solution and lead. The structure of these alloys is very similar to the structure of the lead-cadmium alloys.

The curve for electrical conductivities by Matthiessen [105] is very steep between 100 and 97 per cent. silver. This is the region

[105] Matthiessen: *Pogg. Ann.*, 110. 212, 1860.

in which a solid solution of lead in silver is formed. For alloys containing less than 50 per cent. silver the curve becomes nearly a straight line, which is characteristic of mechanical mixtures of two crystalline phases.

FIG. 32.




**METALS FORMING COMPOUNDS WITH EACH OTHER.**

*Tellurium-Tin.*

The freezing point curve (Fig. 32) by Fay [106] gives the intermetallic compound TeSn, with a eutectic on either side. The results of Kobayashi [107] are in agreement with those of Fay. Alloys containing less than 48 per cent. tin are mechanical mixtures of tellurium; the compound TeSn and those containing

[106] Fay: *Jour. Amer. Chem. Soc.*, 29, 1265, 1907.

[107] Kobayashi: *Zeit. anorg. Chem.*, 69, 1, 1911.

more than 48 per cent. tin are mechanical mixtures of tin and the compound TeSn.

The thermoelectric powers and the electrical conductivities in Fig. 32 are by Haken [108] and the magnetic susceptibilities from the work of Honda and Sone.[109] The compound is indicated on each of the curves. The curve for magnetic susceptibilities consists of two straight lines which intersect at the concentration giving the compound TeSn. One of these straight lines corresponds to mixtures of tellurium and TeSn and the other to mixtures of tin and TeSn. Between 55 and 100 per cent. tin the thermoelectric power curve is a straight line of small slope.

### *Bismuth-Tellurium.*

The freezing point curve of this system (Fig. 33) by Monkemeyer [110] indicates the compound $Bi_2Te_3$ with a eutectic on either side. Alloys to the left of the compound are mixtures of Bi and $Bi_2Te_3$ and those to the right are mixtures of Te and the compound $Bi_2Te_3$.

The thermoelectric power and the electrical conductivity are taken from the observations of Haken,[111] the Hall constant at room temperature from Trabacci [112] and the magnetic susceptibility from the work of Honda and Sone.[113] The presence of the compound is clearly marked on each of the curves. The curve for the Hall constant is very similar to the curve for the thermoelectric powers. A proportionality between the Hall constants and the thermoelectric powers has been recognized by Beattie and these curves are in agreement with the suggestion. Beside the work of Honda and Sone on the diamagnetic susceptibility of these alloys there is some earlier work by Mendenhall and Lent [114] who failed to find in their curve an indication of the compound. Honda and Sone point out that this was probably due to the fact

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[108] Haken: *Ann. d. Phys.*, **32**, 291, 1910.

[109] Honda and Sone: *Sci. Repts. Imp. Univ. Tokio*, **2**, 10, 1913.

[110] Monkemeyer: *Zeit. anorg. Chem.*, **46**, 415, 1905.

[111] Haken: *Ann. d. Phys.*, **32**, 291, 1910.

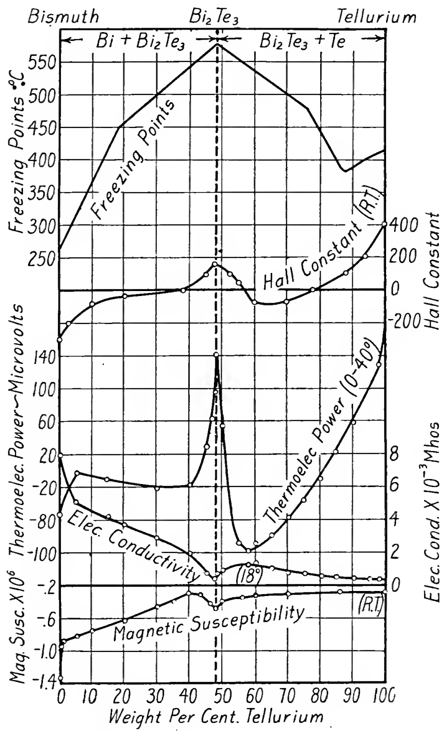
[112] Trabacci: *Nuovo Cim.*, **9**, 95, 1915.

[113] Honda and Sone: *Sci. Repts. Imp. Univ. Tokio*, **2**, 12, 1913.

[114] Mendenhall and Lent: *Phys. Rev.*, **32**, 406, 1911.

that Mendenhall and Lent did not take the points in the neighborhood of the compound close enough together. Between 1 and 41 per cent. tellurium and between 60 and 100 per cent. tellurium the susceptibility curve is nearly a straight line which is characteristic of mechanical mixtures.

FIG. 33.




*Bismuth-Magnesium.*

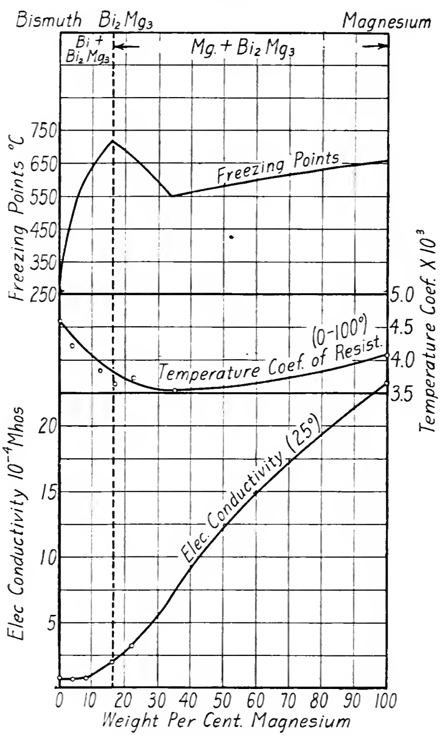
The freezing point curve (Fig. 34) by Grube [115] gives one compound $Bi_2Mg_3$ and one eutectic for this combination of metals. Another eutectic is probably formed between bismuth and the compound $Bi_2Mg_3$, but the temperature of this eutectic nearly coincides with the melting point of bismuth. Alloys to the left of the compound consist of heterogeneous mixtures of bismuth

[115] Grube: *Zeit. anorg. Chem.*, 49, 85, 1906.

and the compound $Bi_2Mg_3$ and those to the right of mixtures of magnesium with the compound $Bi_2Mg_3$.

The electrical conductivity and the average temperature coefficient have been determined by Stepanow.[116] Neither of these curves show the presence of the compound $Bi_2Mg_3$. This may be due to the fact that the points in the neighborhood of this

FIG. 34.




compound were not taken sufficiently close together. The course of the curves on either side of the compound somewhat resembles straight lines, indicating that the alloys on the two sides of the compound are mechanical mixtures.

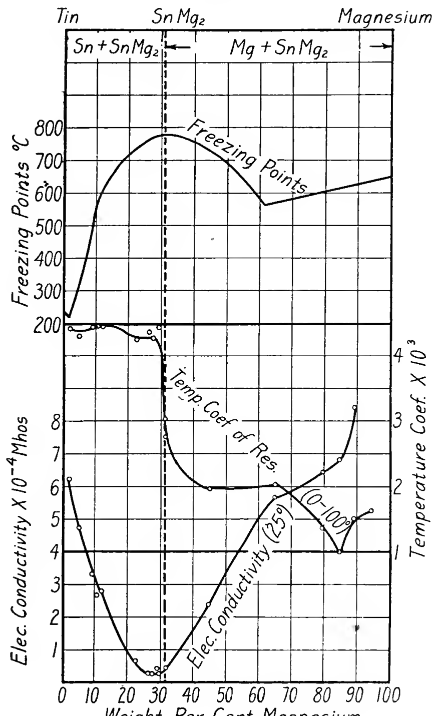
## *Magnesium-Tin.*

The equilibrium diagram for magnesium and tin shows one

[116] Stepanow: *Zeit. anorg. Chem.*, 78, 1, 1912.

intermetallic compound, $Mg_2Sn$. There is a eutectic on either side of this compound. The freezing point curve of Fig. 35 is by Grube.[117] Magnesium does not seem to be soluble in tin, but Grube finds that magnesium dissolves about 6 per cent. of tin. With the exception of alloys in this region, the alloys of this series are mechanical mixtures of two crystalline phases.

FIG. 35.

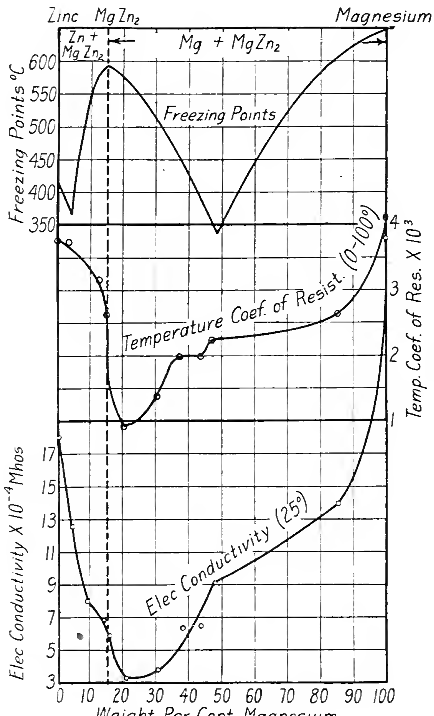



The electrical conductivities and the temperature coefficients of the resistance are known from the work of Stepanow.[116] The addition of tin to magnesium causes a rapid drop in the electrical conductivity and the temperature coefficient. The steepness of these curves for large concentrations of magnesium confirms the existence of solid solutions of magnesium and tin where the concentration of tin is small. The compound is marked by a rapid

[117] Grube: *Zeit. anorg. Chem.*, 46, 1905.

drop in the temperature coefficient and a minimum in the electrical conductivity. Between 0 and about 28 per cent. and between 40 and 65 per cent. magnesium the temperature coefficient is nearly constant. This constancy could be inferred from the fact that the alloys over these regions are mechanical mixtures, in the former case of tin and the compound $SnMg_2$ and in the latter case of the

FIG. 36.




compound $SnMg_2$ and a saturated solid solution of magnesium and tin.

## *Magnesium-Zinc.*

These two metals, according to Grube,[118] from whose work the freezing point curve of Fig. 36 is taken, form one intermetallic compound with the formula $MgZn_2$. On either side of

[118] Grube: *Zeit. anorg. Chem.*, 49, 80, 1906.

this compound is a eutectic and the alloys to the left of the compound may be regarded as heterogeneous mixtures of zinc and the compound $MgZn_2$ and those to the right of the compound, mixtures of magnesium and the compound $MgZn_2$. It seems possible that zinc may form dilute solid solutions with magnesium.

The electrical conductivities and the temperature coefficients of the resistance are from the observations of Stepanow.[119] These curves are similar in form to the corresponding curves for magnesium-tin alloys. In the region where the concentration of zinc is small and dilute solid solutions of zinc in magnesium may be formed both of these curves are steep, especially the curve of electrical conductivities. The position of the compound is marked by a rapid decrease in both the temperature coefficient and the electrical conductivity.

### *Bismuth-Thallium.*

The freezing point curve by Chickashige[120] (Fig. 37) indicates a compound at the concentration corresponding to $Bi_5Tl_3$ with a eutectic on either side of it. The freezing point curve seems to have three maxima, but only one of them corresponds to a simple atomic ratio, and that is the one giving the compound $Bi_5Tl_3$. A micrographic examination also locates a compound in this neighborhood.

The electrical conductivity curve for these alloys are by Whitford[121] and the magnetic susceptibilities by Mendenhall and Lent.[122] Both the electrical conductivity and the magnetic susceptibility were measured at room temperature. The presence of the intermetallic compound is clearly indicated on both of these curves.

### *Aluminium-Magnesium.*

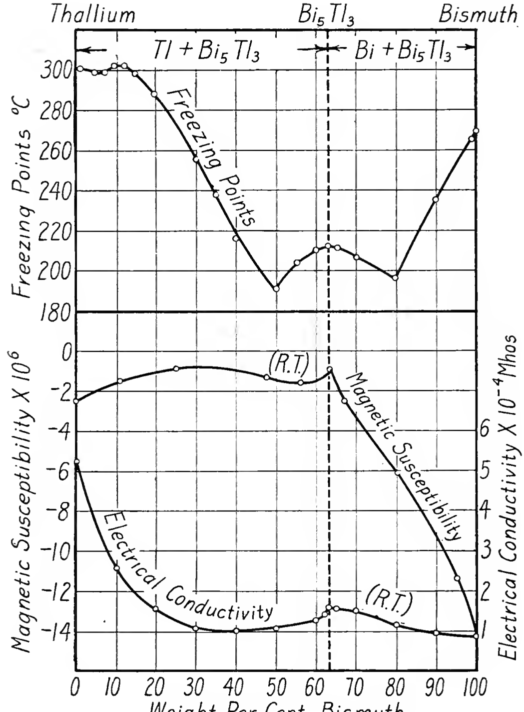
Grube[123] whose freezing point curve is reproduced in Fig. 38 finds one maximum which corresponds to either $Al_2Mg_3$ or $Al_3Mg_4$. These compounds lie so close together that it is difficult to choose between them, but Grube concludes that $Al_3Mg_4$ is the more prob-

[119] Stepanow: *Zeit. anorg. Chem.*, **78**, 25, 1912.
[120] Chickashige: *Zeit. anorg. Chem.*, **51**, 328, 1906.
[121] Whitford: *Phys. Rev.*, **35**, 144, 1912.
[122] Mendenhall and Lent: *Phys. Rev.*, **32**, 415, 1911.
[123] Grube: *Zeit. anorg. Chem.*, **45**, 225, 1905.

able. To the right of this compound the alloys may be considered mechanical mixtures of Mg and the compound $Al_3Mg_4$ and for lower concentrations of magnesium they are mechanical mixtures of aluminium and the compound $Al_3Mg_4$.

Besides the observations of Broniewski[124] from which the

FIG. 37.



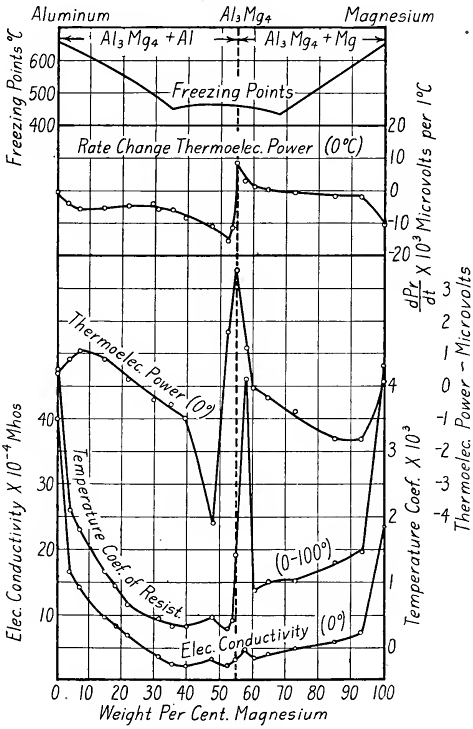

curves in Fig. 38 have been plotted there are observations by Pecheux[125] on the thermoelectromotive forces of some members of this series. According to the interpretation of Broniewski, two compounds are indicated by his curves: *viz.*, AlMg and $Al_2Mg_3$. Of these compounds $Al_2Mg_3$ is much more clearly marked than the compound AlMg.

[124] Broniewski: *Ann. de Phys. et Chem.* (8), 25, 76, 1912.
[125] Pecheux: *C. R.*, 139, 1202, 1904.

*Copper-Arsenic.*

The freezing point curve of Fig. 39 is by Friedrich.[126] From the equilibrium diagram and from a metallographic study of these alloys it is found that copper and arsenic form two compounds $Cu_3As$ and $Cu_3As_2$ and that arsenic dissolves in copper up to 4 per cent.

FIG. 38.




Some observations on the electrical conductivity of copper-arsenic alloys have been made by Matthiessen and Holtzmann[127] and later by Hampe.[128] Friedrich also gives some data on the electrical resistance of these alloys for low concentrations of arsenic. The specific resistance of these alloys and the tempera-

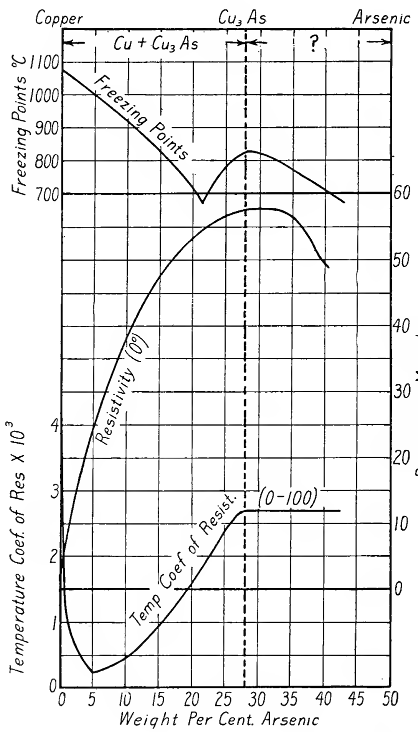
[126] Friedrich: *Metallurgie*, 5, 529, 1908.

[127] Matthiessen and Holtzmann: *Pogg. Ann.*, 110, 229, 186c.

[128] Hampe: *Chemiker, Ztg.*, 726, 1892.

ture coefficient (Fig. 39) are the values given by Puschin and Dischler.[129] The electrical resistance of copper is much increased by the addition of small quantities of arsenic, and the temperature coefficient is decreased. This occurs in the region where a solid solution of arsenic in copper is formed and is characteristic of the formation of such solutions. When the concentration of arsenic is about 28.5 per cent. the specific resistance has its maximum

FIG. 39.



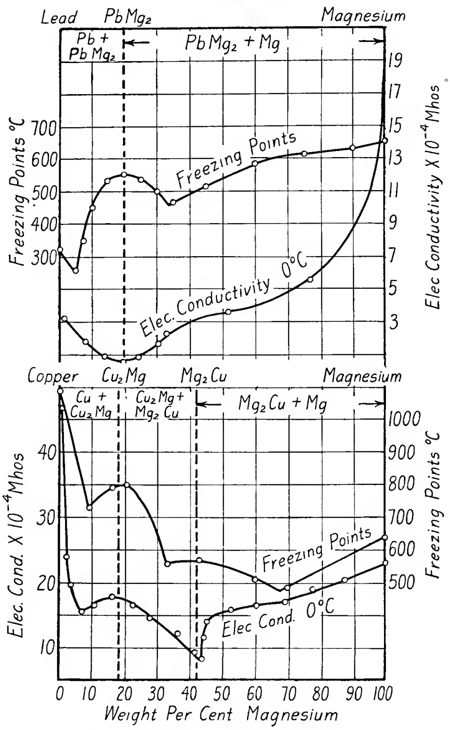

value. This maximum value comes at the concentration for the compound $Cu_3As$. The temperature coefficient decreases from its value in pure copper, passes through a minimum for 6 per cent. arsenic and then increases until the concentration corresponding to the compound $Cu_3As$ is reached. Beyond this concentration the temperature coefficient remains nearly constant.

[129] Puschin and Dischler: *Zeit. anorg. Chem.*, **80**, 65, 1913.

*Lead-Magnesium.*

The freezing point curve [130] (Fig. 40) shows a maximum corresponding to the compound $Mg_2Pb$ with a eutectic on either side. For concentrations of magnesium less than that corresponding to the compound the alloys are heterogeneous mixtures of lead and

FIG. 40.




$Mg_2Pb$ and for greater concentrations they are mixtures of the compound $Mg_2Pb$ and magnesium.

The curve for electrical conductivities by Stepanow [131] (Fig. 40) shows that the electrical conductivity decreases rapidly with the addition of lead to magnesium until the alloy contains about 5 per cent. lead. At the concentration corresponding to the compound $Mg_2Pb$ the electrical conductivity passes through a minimum.

[130] Grube: *Zeit. anorg. Chem.*, **44**, 117, 1905.

[131] Stepanow: *Zeit. anorg. Chem.*, **78**, 12, 1912.

### *Magnesium-Copper.*

The freezing point curve (Fig. 40) as determined by Urasow [132] and also Sahem [133] shows two maxima corresponding to the intermetallic compounds $Cu_2Mg$ and $CuMg_2$. There are, therefore, in the equilibrium four types of crystalline substances to be considered: Cu, $Cu_2Mg$, $CuMg_2$ and Mg. None of these substances seems able to form solid solutions with any of the others. The alloys then become divided into three groups, mixtures of Cu with $Cu_2Mg$; mixtures of $Cu_2Mg$ with $CuMg_2$ and mixtures of Mg and $CuMg_2$.

The electrical conductivity has been measured by Stepanow.[134] He also gives data from which the temperature coefficient can be calculated. These data are, however, very irregular and have not been plotted. Between 100 and 45 per cent. magnesium the curve is nearly a straight line, as it should be for a mechanical mixture of Mg and $CuMg_2$. Between 43 and 20 per cent. magnesium it is again a straight line corresponding to the mixture of $CuMg_2$ and $Cu_2Mg$. The early part of the curve for small concentrations of magnesium is steep and suggests a solid solution rather than a mechanical mixture.

### *Antimony-Tellurium.*

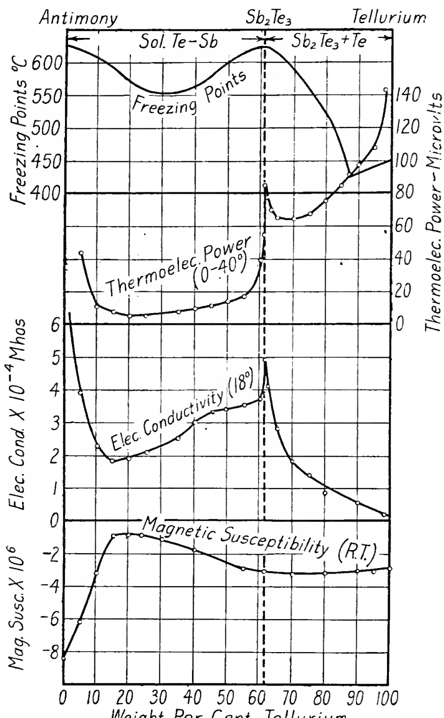
The freezing point curve of this series by Fay and Ashley [135] (Fig. 41) gives a maximum corresponding to the compound $Sb_2Te_3$. There is also a eutectic for which the temperature is 421° C. The compound forms a continuous series of mixed crystals with antimony but does not mix in the same way with pure tellurium.

The electrical conductivity and the thermoelectric power for this series have been measured by Haken.[136] The addition of tellurium to antimony causes a rapid decrease in both the electrical conductivity and the thermoelectric power. Both of these quantities pass through a minimum and rise rapidly to their value for the compound $Sb_2Te_3$. The course of these curves between 0 and 60 per cent. tellurium is typical of alloys formed of two crystalline

[132] Urasow: *Jour. russ. Chem. Ges.*, **39**, 1566, 1909.
[133] Sahem: *Zeit. anorg. Chem.*, **57**, 3, 1908.
[134] Stepanow: *Zeit. anorg. Chem.*, **78**, 20, 1912.
[135] Fay and Ashley: *Amer. Chem. Jour.*, **27**, 1902.
[136] Haken: *Ann. d. Phys.*, **32**, 291, 1910.

phases, forming solid solutions. The compound is clearly marked on both curves. The magnetic susceptibility of these alloys has been studied by Honda.[137] Between 100 and 62 per cent. tellurium the curve is nearly a straight line. Over this region the susceptibility varies little. The compound is marked by a sudden change in the direction of the curve at the concentration of the compound.

FIG. 41.




*Antimony-Aluminium.*

The freezing point curve (Fig. 42) by Gautier[138] has two maxima. One corresponds to the compound AlSb, but the existence of a second compound is questioned.

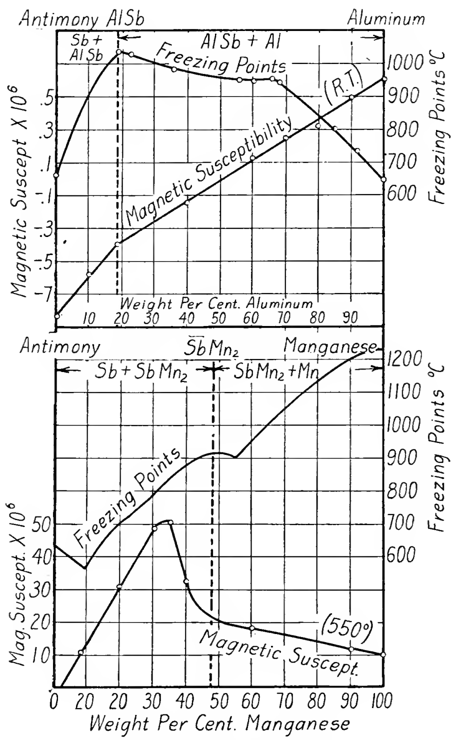
The diamagnetic susceptibility of these alloys has been con-

[137] Honda: *Sci. Rept. Imp. Univ. Tokio*, 2, 9, 1913.

[138] Gautier: "Contribution a l'etude des alleages," 112, 1901.

tributed by Honda.[139] The curve showing the susceptibility as a function of the concentration is made up of two straight lines which intersect where the alloy contains 18.4 per cent. aluminium, *i.e.*, at the concentration for the compound AlSb. The character of the susceptibility curve indicates that alloys containing less than 18.4 per cent. aluminium are mechanical mixtures of anti-

FIG. 42.




mony and the compound AlSb, and those containing more than 18.4 per cent. aluminium are mixtures of aluminium and the compound AlSb.

*Antimony-Manganese.*

The compound $SbMn_2$ is indicated on the freezing point curve (Fig. 42) by Williams.[140] Between 100 and about 52 per cent.

[139] Honda: *Sci. Rept. Imp. Univ. Tokio*, 2, 9, 1913.

[140] Williams: *Zeit. anorg. Chem.*, 55, 1, 1907.

manganese the alloys are heterogeneous mixtures of Mn and the compound $SbMn_2$; between 0 and about 31 per cent. manganese they are a mixture of antimony and a secondary crystalline phase.

The thermal and electrical properties of these alloys have not been studied. The magnetic susceptibility at 550° C. has been determined by Honda.[139] His observations were made with a field of 10.9 kilogausses. The susceptibility for this temperature is nearly independent of the temperature. From 0 to 31.2 per cent. manganese the susceptibility is nearly a linear function of the concentration. In this region the alloys are mechanical mixtures of Sb and $SbMn_2$. Between 31.2 and 40.7 per cent. manganese the character of the susceptibility curve changes because a new crystalline phase appears. Between 40.7 and 47.8 per cent. Mn there is another straight line portion, followed by another linear portion from 50.5 to 100 per cent. Mn, the region over which the alloys are heterogeneous mixtures of manganese and a second crystalline phase.

*Antimony-Zinc.*

The freezing point curve for this series as determined by Monkmeyer [141] (Fig. 43) has two maxima, one corresponding to the compound SbZn and the other to the compound $Sb_3Zn_2$. The alloys divide themselves into three groups—heterogeneous mixtures of Zn and $Sb_3Zn_2$, mixtures of $Sb_3Zn_2$ and SbZn and mixtures of SbZn and Sb. The structure of the series of alloys is very similar to the structure of the antimony-cadmium series.

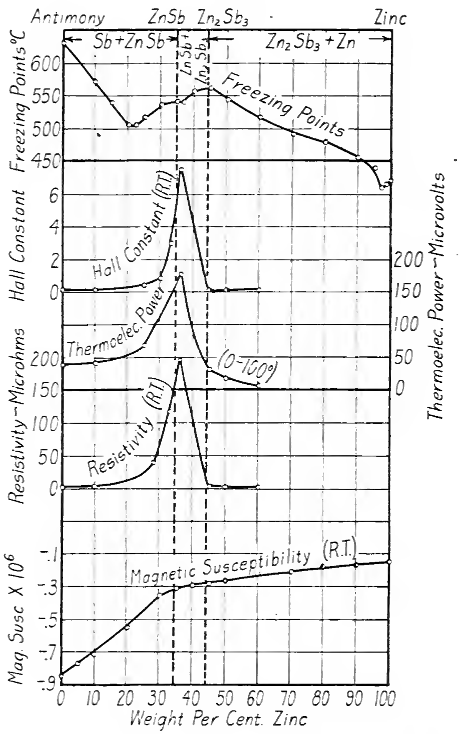
The curve for the magnetic susceptibilities by Honda [142] consists essentially of two straight lines intersecting at the concentration for the compound SbZn. Over the region where there is supposed to be a mixture of $Sb_3Zn_2$ and SbZn the curve departs somewhat from a straight line. The linear relation between the susceptibility and the concentration confirms the existence of the mechanical mixtures indicated by thermal analysis. The curves for the specific resistance, the thermoelectric power and the Hall constant [143] show clearly the compound SbZn, but they give no evidence of the compound $Sb_3Zn_2$.

[141] Monkmeyer: *Zeit. anorg. Chem.*, **43**, 182, 1905.
[142] Honda: *Sci. Rept. Imp. Univ. Tokio,* **2**, 6, 1913.
[143] Smith: *Phys. Rev.*, **32**, 178, 1911.

*Antimony-Cadmium.*

The freezing point curve (Fig. 44) by Treitschke [144] gives a compound SbCd which is stable and another $Sb_2Cd_3$ which is probably unstable. Between 0 and about 40 per cent. antimony the alloys are mixtures of Cd and $Sb_2Cd_3$; between 40 and 52 per

FIG. 43.




cent. mixtures of SbCd and $Sb_2Cd_3$ and between 52 and 100 per cent. mixtures of SbCd and Sb.

The curves for the specific resistance, temperature coefficient and thermal conductivity are from the observations of Eucken and Gehlhoff.[145]

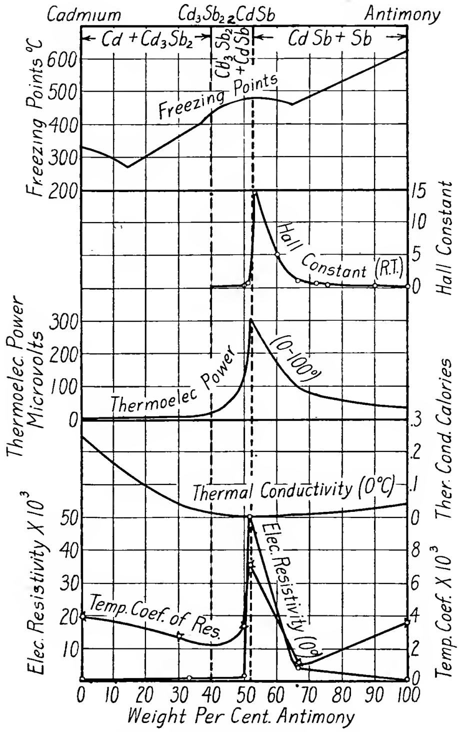
The thermoelectric power of this series has been frequently studied. The curve of thermoelectric powers in Fig. 44 is from

[144] Treitschke: *Zeit. anorg. Chem.*, 50, 217, 1906.

[145] Eucken and Gehlhoff: *Verh. d. deut. Phys. Ges.*, 169, 1912.

Haken.[146] The Hall constant is by the author.[147] The position of the compound is very evident on all of these curves except the curve for the thermal conductivities. On either side of this compound and at some distance from the concentration at which it appears neither the resistance, nor the thermoelectric power, nor

FIG. 44.




the Hall constant changes rapidly with a change in the composition of the alloys.

*Magnesium-Silver.*

The freezing point curve [148] (Fig. 45) gives one maximum at the concentration for the compound MgAg. There is probably a second compound $Mg_3Ag$. Between 0 and 8.5 per cent. magnesium

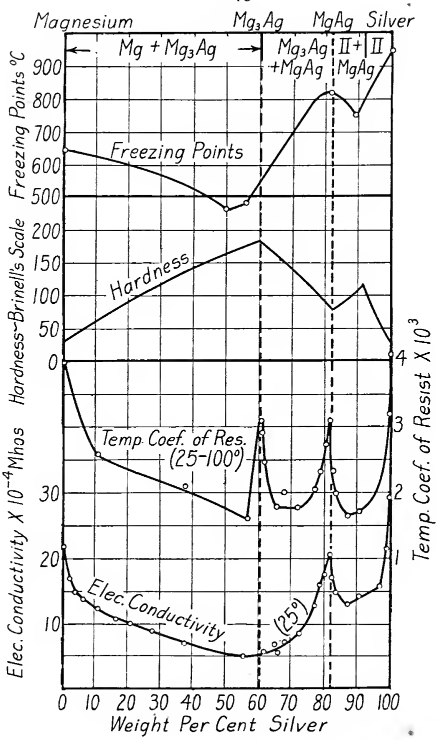
[146] Haken: *Ann. d. Phys.*, 32, 291, 1910.

[147] Smith: *Phys. Rev.*, 32, 178, 1911.

[148] Zemczuzny: *Zeit. anorg. Chem.*, 49, 403, 1906.

there is a solid solution of magnesium in silver followed by a mechanical mixture of this solid solution and the compound MgAg. There then follows a region in which there is a mixture of $Mg_3Ag$ and MgAg. Between 0 and 60 per cent. silver the alloys are mixtures of Mg and $Mg_3Ag$.

FIG. 45.

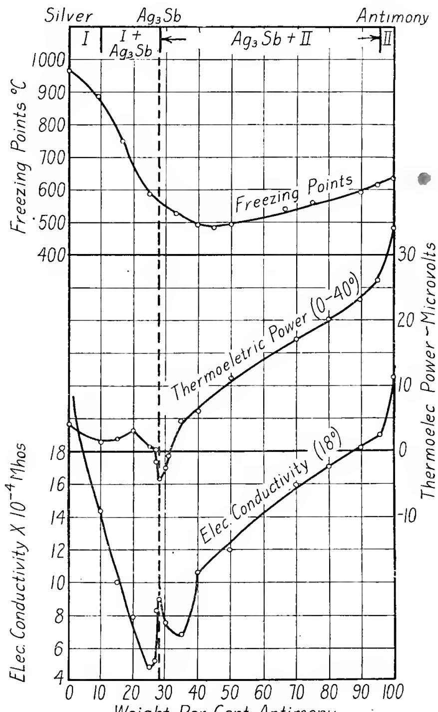



The curve for the hardness [149] of these alloys shows these regions quite clearly. It is made up of four straight lines. One of these lines extends from 0 to 60 per cent. silver, over the region in which the alloys are mechanical mixtures of Mg and $Mg_3Ag$; the next from 60 to 82 per cent. silver where there is a mixture of MgAg and $Mg_3Ag$; the third one from 82 to 91 per cent. silver where there is a mixture of MgAg and a saturated solid solution of magnesium in silver; the last from 91 to 100 per cent. silver, the region of the solid solutions of magnesium in silver. The

[149] Desch: "Intermetallic Compounds," p. 15.

curves for the electrical conductivity and the temperature coefficient are by Smirnow and Kurnakow.[150] The positions of both compounds are marked on these curves. The initial rapid decrease in the electrical conductivity and the temperature coefficient for fairly

FIG. 46.




small concentrations of magnesium in silver is in agreement with the conception that solid solutions are formed over this interval. The nearly linear course of these curves between 10 and 58 per cent. silver follows from the fact that the alloys are mechanical mixtures of two crystalline phases over this interval.

### *Silver-Antimony.*

Petrenko[151] gives the freezing point curve (Fig. 46). By a sudden change in curvature it suggests the compound $Ag_3Sb$. A

[150] Smirnow and Kurnakow: *Zeit. anorg. Chem.*, 72, 31, 1911.

[151] Petrenko: *Zeit. anorg. Chem.*, 50, 1906.

solid solution of silver in antimony is formed until the concentration of the silver becomes about 4 per cent. and a solid solution of antimony in silver until the concentration of antimony is about 10 per cent. Between about 10 and 28 per cent. antimony there is a mechanical mixture of $Ag_3Sb$ and a saturated solid solution of antimony in silver and between 28 and 96 per cent. a mixture of $Ag_3Sb$ and a saturated solution of silver in antimony.

The curve for the thermoelectric heights as well as that for the electrical conductivities has been worked out by Haken,[152] and these curves are reproduced in Fig. 46. The compound is clearly indicated and the region in which silver is soluble in antimony is marked by the steepness of both curves in this region. In like manner the interval in which antimony is soluble in silver is indicated by the characteristic drop in the electrical conductivity. The decrease in the thermoelectric power for small concentrations of antimony is less marked.

*Aluminium-Copper.*

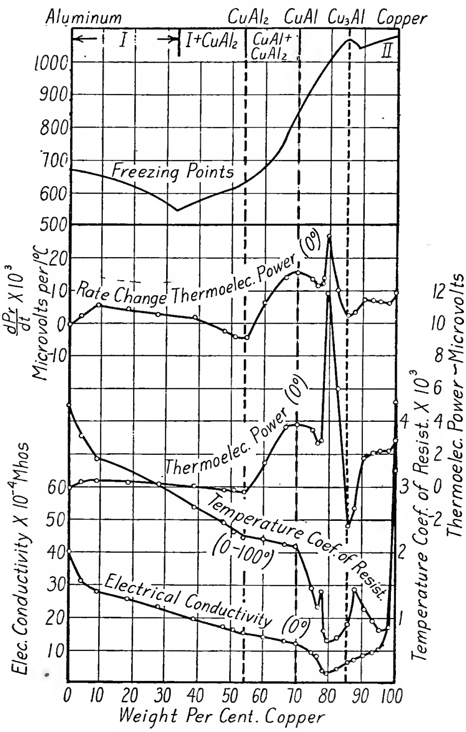
By thermal analysis Gwyer [153] finds evidence of three compounds: $Al_2Cu$, AlCu and $AlCu_3$ (Fig. 47). The compound $Al_2Cu$ is decomposed before fusion. Between 0 and 9 per cent. copper there are solid solutions of aluminium in copper, followed by a region of mixed crystals of $Cu_3Al$ and CuAl; a second region of mixtures of CuAl and $CuAl_2$, and a third region of mixtures of $CuAl_2$ and a saturated solution of copper in aluminium.

A number of observations have been made on the electrical properties of these alloys. Among the earlier observations in this region are those made by LeChatelier,[154] Dewar and Flemming,[155] Battelli,[156] Steinmann,[157] Pouchine [158] and Pecheux.[159] The curves in Fig. 47 have been plotted from the data given by Broniewski.[160] On the curve for electrical conductivity and also on the one for the temperature coefficient the three compounds are indicated by a

[152] Haken: *Ann. d. Phys.*, 32, 291, 1910.
[153] Gwyer: *Zeit. anorg. Chem.*, 57, 113, 1908.
[154] LeChatelier: *C. R.*, 101, 454, 1890.
[155] Dewar and Flemming: *Phil. Mag.* (5), 36, 271, 1893.
[156] Battelli: *Atti. R. Inst. Veneti.* (6), 5, 1148, 1886–7.
[157] Steinmann: *C. R.*, 130, 1300, 1900.
[158] Pouchine: *Jour. Soc. phys. Chem. russ.*, 39, 528, 1907.
[159] Pecheux: *C. R.*, 148, 1041, 1909.
[160] Broniewski: *Ann. de Phys. et Chem.* (8), 25, 91, 1912.

change in the slope of the curves at the concentrations corresponding to the compounds. On the curve for the thermoelectric power and also on the curve for the variations of the thermoelectric power with the temperature the compounds $Al_2Cu$ and $AlCu_3$ are marked by minima in the curves. Over the region between 91 and 100 per cent. copper where solid solutions of aluminium in copper

FIG. 47.




are formed the electrical conductivity and the temperature coefficient show the decreases characteristic of such solutions.

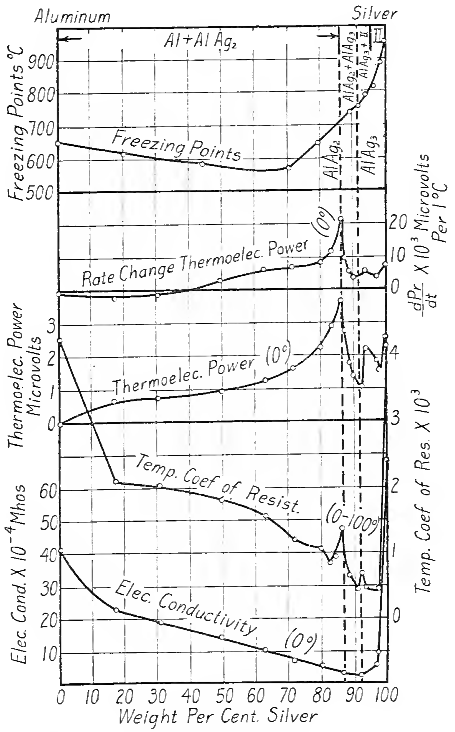
## *Aluminium-Silver.*

The freezing point curve (Fig. 48) by Petrenko [161] gives two compounds, $AlAg_2$ and $AlAg_3$. These compounds are indicated by a change in the curvature of the freezing point curve at the concentration at which the compound occurs. This change in curvature is

[161] Petrenko: *Zeit. anorg. Chem.*, 46, 49, 1905.

not very evident from the curve as plotted in Fig. 48. Between 0 and 87.5 per cent. silver the alloys are mechanical mixtures of aluminium and the compound $AlAg_2$; between 87.5 and 91.5 per cent. silver mixed crystals of $AlAg_2$ and $AlAg_3$; between 91.5 and 94 per cent. silver mixtures of $AlAg_3$ and saturated solid solutions of

Fig. 48.



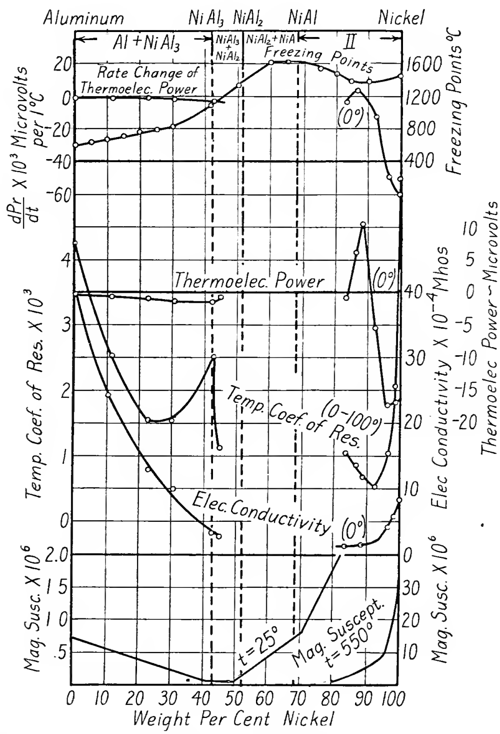

aluminium in silver, and between 94 and 100 per cent. silver solid solutions of aluminium in silver.

The curves for the electrical conductivity, temperature coefficient, thermoelectric power and variations of the thermoelectric power with the temperature have been taken from the observations of Broniewski.[162] The compound $AlAg_2$ is marked clearly by a peak in each of the curves except the curve for the electrical conductivity where the peak is small. On the other hand, a

[162] Broniewski: *Ann. de Phys. et Chem.* (8), **25**, 83, 1912.

minimum occurs in each of the curves except the curve for electrical conductivities where the concentration corresponds to the compound $AlAg_3$. Except for the two peaks in the curve for the temperature coefficient that curve as well as the curve for electrical conductivities has the form which is found in binary alloys

FIG. 49.




of metals which form limited solid solutions with each other and then these solid solutions mix mechanically to form the remainder of the alloys of the series.

## *Aluminium-Nickel.*

The freezing point curve (Fig. 49) by Gwyer [163] gives a maximum near the concentration corresponding to the compound NiAl. Between 0 and 42 per cent. nickel the alloys are mixtures of Al

[163] Gwyer: *Zeit. anorg. Chem.*, 57, 133, 1908.

and $NiAl_3$; between 42 and 52 per cent. nickel mixtures of $NiAl_3$ and $NiAl_2$; between 52 and 68 per cent. nickel mixtures of $NiAl_2$ and NiAl, and between 68 and 100 per cent. nickel an unsaturated solution of aluminium in nickel.

The electrical conductivity, the temperature coefficient, the thermoelectric power and its variation with the temperature have been plotted from the observations of Broniewski.[164] In the interval between 45 and 84 per cent. nickel there are no observations on account of the brittleness of the alloys in this region. The compound $NiAl_3$ is indicated by a peak on the temperature coefficient curve. The magnetic susceptibilities by Honda [165] have been measured at 25° C. for alloys containing less than 80 per cent. nickel. For alloys containing more than 80 per cent. nickel the susceptibilities were determined at 550° C. A magnetic field of from 5 to 12 kilogausses was used. Until the alloys contain 80 per cent. nickel the susceptibility curve consists of four straight lines intersecting at the concentrations at which a new crystalline phase appears.

### *Nickel-Tin.*

The composition of this series of alloys is very complex. The freezing point curve by Gautier [166] has been reproduced in Fig. 50. Five different kinds of crystals are present in the solidified alloys.

No observations have been found on the thermal and electrical properties of these alloys. The magnetic properties have been studied by Honda.[165] On the alloys containing less than 60 per cent. nickel the observations were made at 25° C. On the remainder of the alloys the observations were made at 550° C.—a temperature above the transformation point. The external magnetic field was from 5 to 12 kilogausses. The ferro-magnetic properties disappear when the concentrations of the constituents correspond to the compound $Ni_3Sn$. So long as the alloys are composed of the same two kinds of crystals in varying concentrations the susceptibility is a linear function of the concentration. Where one type of crystal disappears and is replaced by another the slope of the curve suddenly changes.

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[164] Broniewski: *Ann. de Chem. et Phys.* (8), **25**, 108, 1912.

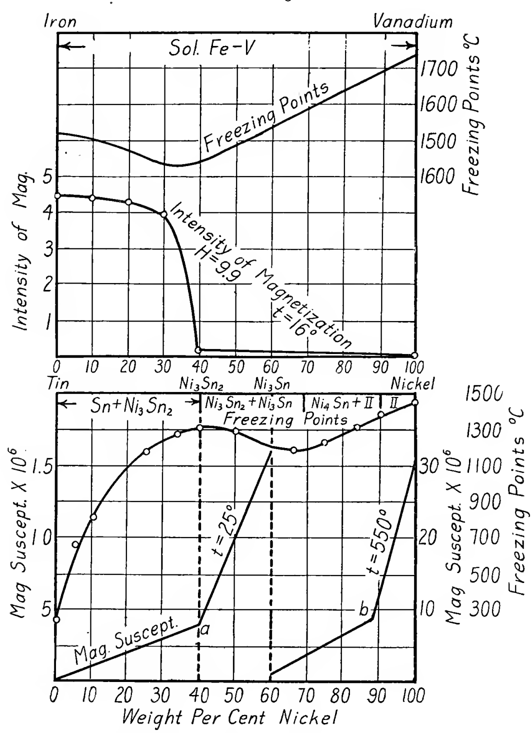
[165] Honda: *Ann. d. Phys.*, **32**, 1015, 1910.

[166] Gautier: *C. R.*, **122**, 109.

*Iron-Vanadium.*

The composition of iron and vanadium alloys has been studied by Vogel and Tammann,[167] and it has been found that they solidify in the form of an unbroken series of mixed crystals. The freezing point curve (Fig. 50) has a minimum in the neighborhood of 35 per cent. vanadium.

FIG. 50.



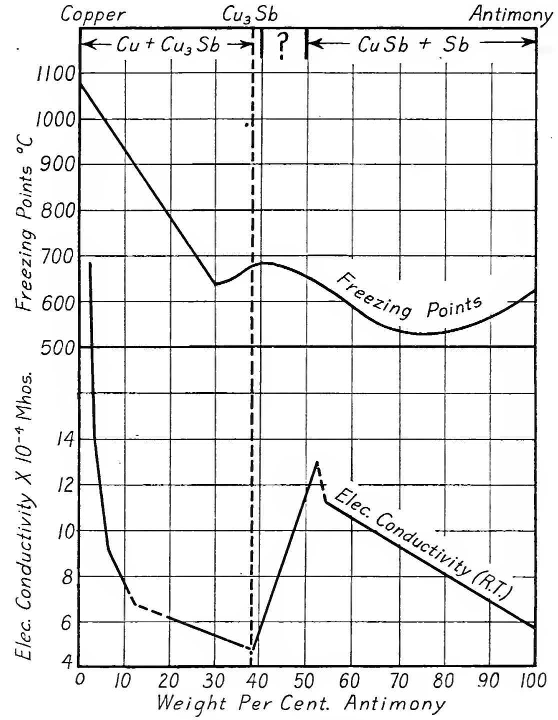

The electrical and thermal properties of this series of alloys do not seem to have been studied. There are observations by Honda[168] on the intensity of magnetization. These observations were made at 16° C. and with a magnetic field of 9.9 gausses. The intensity of magnetization of iron decreases slowly with an increasing concentration of vanadium until that concentration is

[167] Vogel and Tammann: *Zeit. anorg. Chem.*, **58**, 79, 1908.

[168] Honda: *Ann. d. Phys.*, **32**, 1910, 1912.

reached at which the freezing point curve has its minimum. Here there is an extraordinarily rapid decrease in the intensity of magnetization so that an alloy containing more than 40 per cent. of vanadium is very feebly magnetic.

FIG. 51.




*Copper-Antimony.*

Baikow [169] has given a complete equilibrium diagram from which the freezing point curve (Fig. 51) is taken. The compound $Cu_3Sb$ is formed. Alloys to the right or left of this compound are heterogeneous mixtures of two crystalline phases. Copper, according to Stead, dissolves about 0.3 per cent. antimony.

For small concentrations of antimony the electrical conductivity curve by Matthiessen [170] is very steep. This is in the region

[169] Baikow: *Jour. reiss. Phys. Chem. Ges.*, 36, 111, 1904.

[170] Matthiessen: *Pogg. Ann.*, 110, 190, 1860.

where antimony and copper form dilute solid solutions. The electrical conductivity curve shows a sudden change in direction where the concentrations correspond to the compound $Cu_3Sb$. Between 55 and 100 per cent. antimony the conductivity curve is a straight line. Over this interval the alloys are mechanical mixtures. A third region of mechanical mixtures is indicated by the straight line representing the electrical conductivity between 38.4 and 52 per cent. antimony.

### CHANGE OF THERMOELECTROMOTIVE FORCE WITH TEMPERATURE.

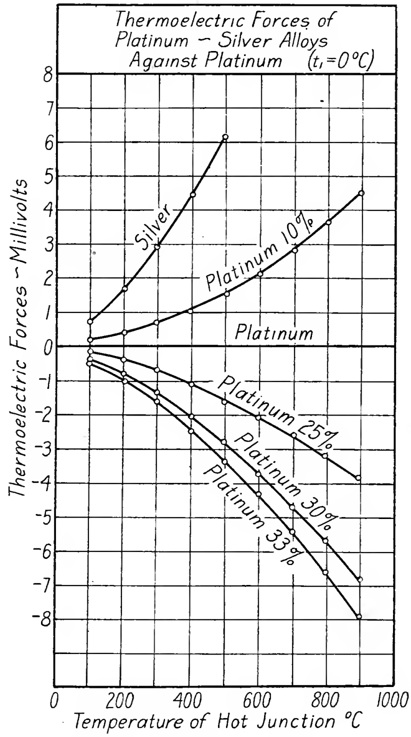
The rate of variation of the thermoelectromotive force with the temperature for a large number of aluminium alloys has already been discussed. The observations on these alloys were made by Broniewski. In his work the observations were extended over a limited range of temperature. The most important work in this connection is that of Giebel,[171] in which the observations were extended over a large range of temperature. He studied the following series of alloys: Palladium-gold, palladium-platinum, palladium-silver, platinum-silver, platinum-rhodium, and platinum-iridium. The thermoelectromotive forces were measured against platinum in this case and the temperature of the cold junction was kept at 0° C. Observations were made at intervals of 100° C. between 0° and 900° C. The observed thermoelectromotive forces have been plotted against the temperatures in Figs. 52, 53 and 54. From Figs. 52 and 54 it is seen that the higher the temperature the more rapid is the rate of change of the thermoelectromotive force with the temperature for palladium-silver and for platinum-silver alloys. In the palladium-platinum series (Fig. 53) there is nearly a linear relation between the thermoelectromotive force and the temperature after the alloy contains about 40 per cent. platinum. When the concentration of platinum is increased above 40 per cent. this linear relation is more nearly realized.

In Fig. 55 the thermoelectromotive force in platinum-rhodium alloy at a particular temperature has been plotted against the concentration of rhodium in the alloy. These curves show that the thermoelectromotive force increases rapidly with the increase in the concentration of rhodium until the alloy contains about 5 per cent rhodium. Between 5 and 10 per cent. rhodium the increase is much less rapid, especially at low temperatures. Increasing the

[171] Giebel: *Zeit. anorg. Chem.*, 69, 38, 1910, and 70, 240, 1911.

concentration of rhodium beyond 10 per cent. changes only slightly the thermoelectromotive force until the temperature of the hot junction exceeds 1000° C. At very high temperatures the thermoelectromotive force continues to increase with increasing concentration of rhodium, but this rate of increase decreases with increasing concentration of rhodium.

FIG. 52.




The relation between the thermoelectromotive force and the difference in temperature between the junctions may be expressed by an equation of the form

$$E = a\,t + b\,t^2 + c\,t^3$$

where one junction is kept at 0° C. and the other at $t$° C. For a large number of metals and alloys it has been found that only the second power of the temperature need be considered. The equation then becomes, to a very good approximation,

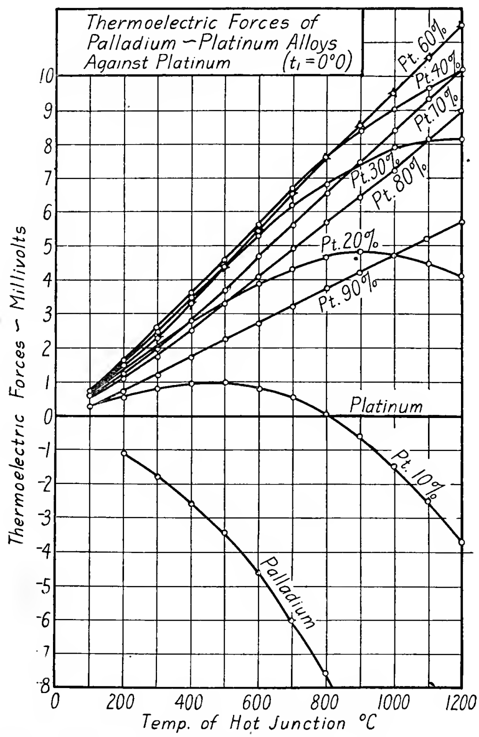
$$E = a\,t + b\,t^2.$$

In such a case the rate of variation of the thermoelectromotive force with the temperature becomes

$$\frac{d\,E}{d\,t} = P = a + 2\,b\,t.$$

This equation states that the thermoelectric power is a linear

FIG. 53.




function of the difference of temperature between the junctions. In some of the platinum-palladium alloys it has already been seen to be independent of the temperature. The rate of variation of the thermoelectric power with the temperature is

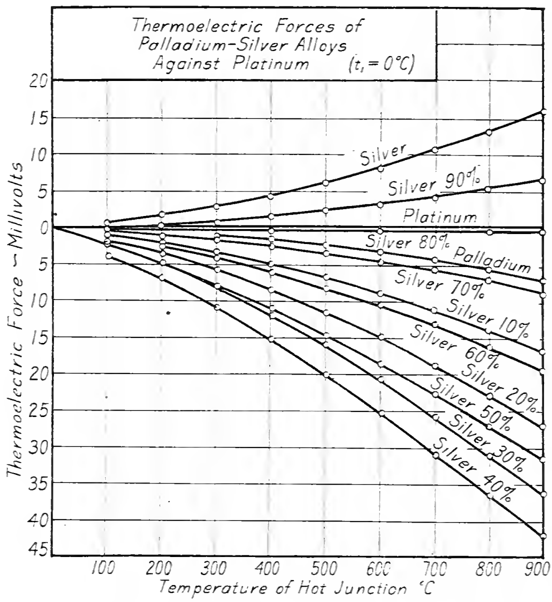
$$\frac{d\,P}{d\,t} = 2\,b.$$

In so far as the approximation introduced above is correct the variation of the thermoelectric power with the temperature is the same for all temperatures.

THEORIES OF RESISTANCE AND THERMOELECTROMOTIVE FORCES.

Lord Rayleigh[172] and Liebenow,[173] independent of each other, came to the conclusion that the increase in specific resistance which alloys show in excess of the resistance calculated from the resist-

FIG. 54.



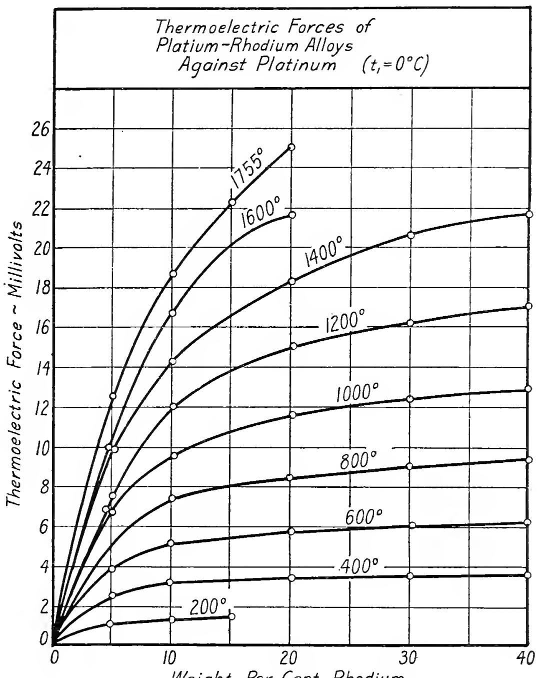

ance of their components may be attributed to the thermoelectromotive forces which arise between the junctions of the metals forming the alloys. According to these theories, the electrical current passing from one layer of metal to another layer of the other metal in the alloy develops or absorbs heat at the surface of contact between the components of the alloy, on account of the Peltier effect. These temperature differences cause thermoelectromotive forces to be set up in the alloy in such a way that they are equivalent to a large number of small cells connected in series, so that they oppose the flow of the current through the substance. They have, therefore, the effect of an added resistance. Since the difference in temperature between the contacts is proportional to the current flowing in the conductor, and since the thermoelectro-

[172] Lord Rayleigh: *Nature*, 54, 154, 1896.

[173] Liebenow: *Zeit. Electrochem.*, 4, 201 and 217.

motive forces are proportional to the difference in temperature, this back electromotive force is proportional to the current. The opposition to the flow of current through the alloy from this cause will, therefore, behave like a resistance and it will be impossible to distinguish between the ordinary resistance and that which arises from these thermoelectromotive forces. It is of importance

FIG. 55.

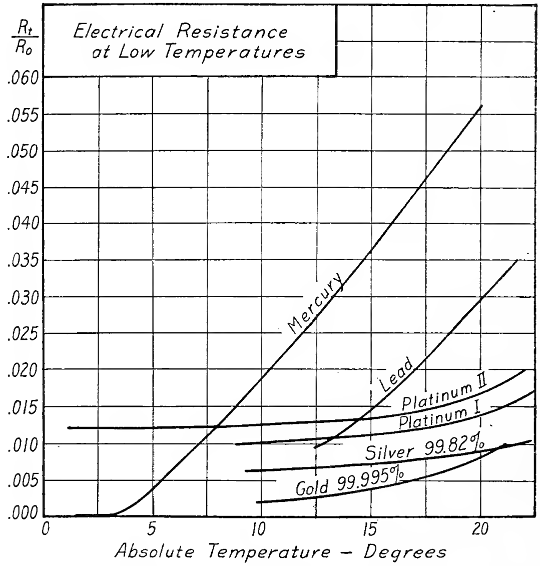



to note that where the constituents form compounds in which the resistance is high, it is necessary on the basis of this theory to assume a thermoelectromotive force between the molecules. Such an assumption is not very probable.

Some evidence for the correctness of this theory is found in the consideration of the way in which the electrical resistance of metals and alloys behaves at extremely low temperatures. When the temperature of a pure metal is decreased, the electrical resist- temperature, until the temperature is 3 or 4 degrees above the ance is found to be very accurately proportional to the absolute

absolute zero where the superconducting state appears and the electrical resistance almost entirely disappears. If, on the other hand, the temperature of an impure metal or alloy is decreased indefinitely, the resistance does not disappear at the absolute zero, but approaches a constant value. This suggests that there is in the resistance of an alloy an added constant term which does not disappear at the absolute zero. The theory of Lord Rayleigh leads at once to the existence of such a term. The added resistance arising from the causes considered in this theory does not seem large enough to account for the very high resistance of some alloys.

FIG. 56.




By reference to Fig. 56 it will be seen that the curve showing the relation between the electrical resistance of mercury and its temperature is nearly a straight line except near the origin. The curve for pure lead is also observed to be a straight line, but the corresponding curves for metals containing small admixtures of other metals do not seem to pass through the origin when prolonged backward. In such cases the electrical resistance seems to approach a constant value which persists to the absolute zero. Such a constant value is to be expected on the basis of the theory proposed by Lord Rayleigh and may, therefore, be taken as par-

tial evidence of the correctness of that theory. From the above point of view it is clear that it is impossible to prepare a good conductor by mixing two or more metals with each other. There will always be present this added resistance which makes the alloy at least not a better conductor than the constituents of which it is composed. Ordinarily the alloy is found to have a lower conductivity than would be calculated from its constituents by the additive law.

This theory of Lord Rayleigh may be stated more fully as follows:

Let $R_0$ = the resistance of the alloy at 0° C.

$\gamma$ = the temperature coefficient of resistance of the alloy.

$R$ = the resistance of the alloy at 0° C. calculated from its constituents by the additive law.

$\alpha$ = the temperature coefficient of the alloy calculated by the additive law.

$R_c$ = the contact resistance occurring at the surface of two metals forming the alloy.

$\beta$ = the temperature coefficient of the constant resistance.

Then,

$$R_0 (l + \gamma t) = R (l + \alpha t) + R_c (l + \beta t).$$

The resistance $R_c$ is, according to Lord Rayleigh and Liebenow, caused by thermoelectromotive forces.

Where it is possible to assume that the temperature coefficients $\gamma$, $\alpha$ and $\beta$ are independent of the temperature, it is possible to write,

$$R_0 = R + R_c, \text{ and } 0^\circ \text{ C.,}$$

and therefore,

$$R_0 \gamma = R \alpha + R_c \beta,$$

at any temperature.

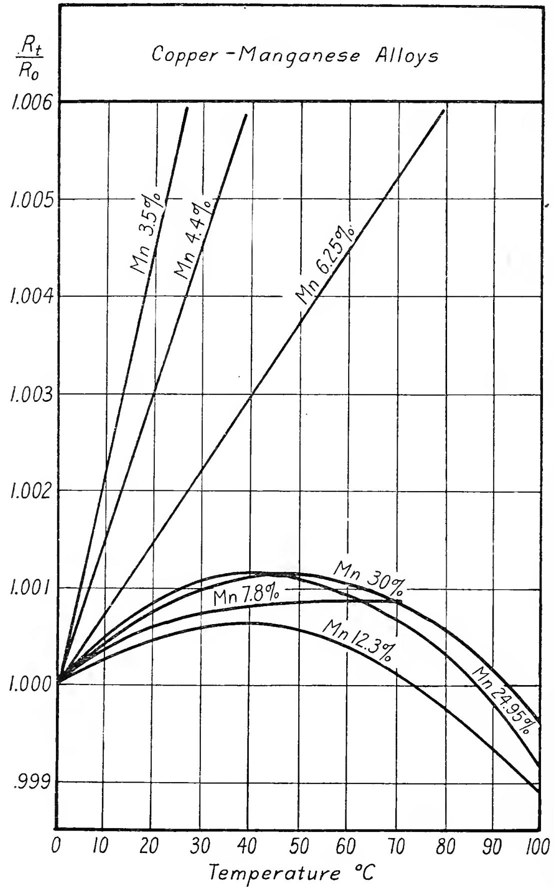
Whence,

$$\gamma = \frac{R\alpha + R_c \beta}{R_0}.$$

From this equation it is seen that $\gamma$ may be negative when $\beta$ is negative and $R_c \beta > R\alpha$. The temperature coefficient of alloys has been found negative in some cases. A well-known example is the case of copper-manganese alloys. Curves showing the ratio of the resistance at any temperature to the resistance at zero for some

copper-manganese alloys have been reproduced in Fig. 57. They are taken from the work of Guertler.[174] For an alloy containing 12.3 per cent. of manganese the temperature coefficient is positive above and negative below 40° C.

FIG. 57.




If it is possible to assume that $\beta = o$, that is, that the contact resistance is independent of the temperature,

$$R_o\,(l + \gamma\, t) = R\,(l + \alpha\, t) + R_c,$$

[174] Guertler: *Jahr. der Rad. und Elekt.*, 5, 17, 1908.

and since

$$R_0 = R + R_c,$$
$$R_0\gamma = R\alpha$$
$$\frac{R_0}{R} = \frac{\alpha}{\gamma}.$$

This equation is equivalent to the empirical rule stated by Matthiessen and Vogt; namely, that the observed temperature coefficient of the resistance divided by that calculated from the additive law is equal to the observed electrical conductivity divided by the electrical conductivity calculated from the additive law. In so far as this rule may be accepted the curve for the electrical conductivity of a series of alloys ought to be the same as the curve for the temperature coefficient of that same series of alloys. In the preceding pages it has been seen that in very many cases there is a parallelism between the curve for the electrical conductivity and that for the temperature coefficient of the resistance. This parallelism offers satisfactory proof of the correctness of this rule in many cases.

The theory of Lord Rayleigh also leads to the second rule stated by Matthiessen and Vogt. Since

$$R_0(+l\gamma t) = R(l + \alpha t) + R_c,$$

and

$$R_0 = R + R_c,$$
$$R_e = R_0 - R =$$

difference between observed and calculated resistance at 0° C., and

$$R_c = R_0(l + \gamma t) - R(l + \alpha t) =$$

the difference between the observed and calculated resistance at $t°$ C. Since each of these differences is equal to the contact resistance which has been assumed independent of the temperature, these differences ought to be the same for all temperatures. In other words, the difference between the observed and the calculated resistance is the same whatever the temperature. The large number of cases in which this rule has been found to be verified gives evidence that the temperature coefficient of the contact resistance is either zero or very small.

The increase in the electrical resistance of solid solutions over the resistance of the pure metals of which they are composed does

not find an easy explanation on the basis of the electron theory of metallic conduction. One assumption which has been made to explain this increase is that the number of free electrons in the alloy is much less than in pure metals. This assumption when considered in connection with Wiedemann and Franz's law does not lead to satisfactory results. The departures from this law, which states that the ratio of the thermal to the electrical conductivity is a constant for any particular temperature, are greater for alloys than for pure metals. These departures are always of such a nature that the electrical conductivity has been decreased more than the thermal conductivity by the formation of the alloy. This, with other considerations, has lead Schenck[175] to suggest that the increase in the electrical resistance of the alloy over the value calculated by the additive law could be accounted for by assuming that it arises from an increase in the frictional resistance which the electrons encounter in their motion through the alloy. This increase in frictional resistance to the motion of the electrons may be thought of as produced in a way very analogous to the way in which on the basis of the kinetic theory the addition of one gas to another causes an increase in the viscosity. Schenck thinks that the slowly diffusing molecules of the added metal hand on their energy and thus participate in the thermal conductivity but not in the process of electrical conduction. For this reason the ratio of the thermal to the electrical conductivity in mixed crystals is greater than for pure metals, and this quotient increases with increasing concentration of the added metal. The ratio of these conductivities in alloys as in pure metals is approximately proportional to the absolute temperature.

According to the electron theory, the different concentration of the electrons in the two metals is the source of a diffusion current which is the cause of the thermoelectromotive force which arises when the junctions of two metals or alloys are at different temperatures.

Let $e$ = the thermoelectromotive force per degree difference in temperature.

$R$ = the gas constant in ergs.

$F$ = 965,450 coulombs.

$N_a$ = number of electrons per cubic centimetre in $A$.

$N_b$ = number of electrons per cubic centimetre in $B$.

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[175] Schenck: *Ann. d. Phys.*, **32**, 261, 1910.

Then,

$$e = \frac{R}{F} \text{Log}_e \frac{N_a}{N_b}.$$

Many alloys give such large values of the thermoelectromotive force against one of the pure metals of which they are composed that in the application of the above equation it is necessary to assume very large changes in the number of free electrons to be produced by adding one metal to the other. In order to avoid these improbable assumptions Schenck has introduced the assumption already referred to—that it is the friction of the free electrons rather than their number that is changed by alloying one metal with another. By using this assumption that there is an increase in the frictional resistance of the electrons in the alloys over the resistance which they experience in pure metals, Schenck has been able to derive a relation between the thermal and electrical conductivity of the alloy, the thermal and electrical conductivity of the pure metallic solvent, and the thermoelectric power of the alloy against the pure solvent.

Let $k$ = thermal conductivity of the pure solvent.

$\sigma$ = electrical conductivity of the pure solvent.

$k'$ = the thermal conductivity of the alloy.

$\sigma'$ = the electrical conductivity of the alloy.

$\pi$ = the thermo-electromotive force of the solid solution against the pure solvent for 1° C. temperature difference between the junctions.

$R$ = the gas constant.

$e$ = the specific electrical charge = 96,540 coulombs.

Then for dilute solutions Schenck shows that

$$\pi = \frac{R}{2e} \text{Log}_e \left( \frac{k'}{\sigma'} \div \frac{k}{\sigma} \right).$$

Some observations have been made by Bernoulli [176] to test the validity of this equation. The following table shows the kind of agreement which exists between the observed and calculated values.

[176] Bernoulli: *Ann. d. Phys.*, 33, 690, 1910.

| Solvent. | Element in solution. | $\pi$ Observed. | $\pi$ Calculated. |
|---|---|---|---|
| Silver ............ | 2.73 per cent. Th. | 2.8 | 2.6 |
| | 4.76 per cent. Th. | 10.3 | 8.4 |
| | 4.00 per cent. Sn. | 7.6 | 8.9 |
| Cadmium......... | 5.14 per cent. Hg. | 2.8 | 2.2 |
| | 10.0 per cent. Hg. | 2.6 | 3.0 |
| Copper ........... | 5.00 per cent. Sn. | 3.4 | 3.6 |
| | 3.11 per cent. Zn. | 2.9 | 3.6 |
| | 5.00 per cent. Zn. | 1.4 | 6.6 |
| | 3.94 per cent. Ni. | 13.3 | 3.9 |
| | 17.30 per cent. Ni. | 27.3 | 11.2 |

From this table it is seen that for dilute solutions fair agreement exists between the observed and the calculated values. The more concentrated the solution the less satisfactory is the agreement.

### RESISTANCE AND HARDNESS.

A theory of electrical conductivity proposed by March[177] offers a possible explanation of the relation between the elastic properties and the electrical conductivity of alloys. According to this theory, the number of free electrons in a metal or alloy, and therefore the electrical conductivity, is in part, at least, determined by the characteristic frequency of vibration of the atoms about their positions of equilibrium. Whatever changes this characteristic frequency would change at the same time the elastic properties and the thermal and electrical properties. On the basis of this theory the number of free electrons decrease with increasing frequency of the characteristic vibration of the atoms. Whatever, therefore, decreases the frequency of the characteristic vibrations of the atoms increases the electrical conductivity of the substance. Hence, at the absolute zero where the characteristic frequency of vibration of the atoms is very small or else disappears, the electrical conductivity will be very large. This is, of course, exactly what is observed in metals at very low temperatures where they pass into the superconducting state.

The formation of a solid solution produces a change in the elastic properties which causes the characteristic frequency of vibration of the atoms to increase. This arises out of the fact

[177] March: *Ann. d. Phys.*, **49**, 710, 1916.

that in an alloy in which the components *A* and *B* form mixed crystals, a molecule of *A* and a molecule of *B* act on each other with greater force than that with which a molecule of *A* acts on a molecule of *A* or a molecule of *B* on a molecule of *B*. There is on this account an increase in the cohesive forces and consequently an increase in the characteristic frequency of vibration of the atoms. With this increase in frequency is associated a decrease in the number of free electrons and a corresponding increase in the electrical resistance. From this point of view it is possible to see that where such elastic properties as hardness or tensile strength have maximum values, the electrical resistance will have a maximum value and the electrical conductivity a minimum value. Many illustrations of this have been seen in the preceding curves.

If the two components *A* and *B* of the alloy are insoluble in each other, the force which the molecule *A* exerts on another molecule *A* or the force which a molecule *B* exerts on another molecule *B* exceeds the force which a molecule *A* exerts on a molecule *B* or that which a molecule *B* exerts on a molecule *A*. Consequently each of these classes of molecules will form a group of crystals and the alloy will be a conglomerate formed of groups of crystals of the two constituents. In such an alloy the characteristics of each constituent are retained and the physical properties are additive. The components will, therefore, retain their characteristic vibrations and their elastic properties as well as the number of free electrons, and the electrical conductivity will change in conformity to the additive law. The hardness which increases with the frequency of the characteristic vibration of the atoms should in such cases be a linear function of the concentration of one of the constituents in the alloy. In such alloys the electrical conductivity will also be a linear function of the concentration of one of the constituents. Many cases of this kind have been noted in the preceding pages. This theory seems to offer a possible explanation of some of the interesting relations noted among the physical properties of alloys. Although the theory may not be satisfactory in many particulars, it is without doubt very suggestive.

Grateful acknowledgment is made to the Engineering Experiment Station of the Ohio State University for generous financial assistance in aid of this work.

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